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U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF CHEMISTRY—BULLETIN No. 99.

H. W. WILEY, Chief of Bureau.

PROCEEDINGS

OF THE

TWENTY-SECOND ANNUAL CONVENTION

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS,

HELD AT

WASHINGTON, D. C., NOVEMBER 16, 17, AND 18, 1905.

EDITED BY

HARVEY W. WILEY,
SECRETARY OF THE ASSOCIATION.

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1906.

LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Chemistry,
Washington, D. C., February 24, 1906.

Sir: I have the honor to transmit for your approval the Proceedings of the Twenty-second Annual Convention of the Association of Official Agricultural Chemists, the discussion and reports having been condensed as far as seemed compatible with a clear presentation of the work done and the action taken. I recommend that this report be published as Bulletin No. 99 of the Bureau of Chemistry.

Respectfully,

H. W. Wiley.
Chief.

Hon. James Wilson,
Secretary of Agriculture.

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PROCEEDINGS OF THE TWENTY-SECOND ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

FIRST DAY.

THURSDAY—MORNING SESSION.

The twenty-second annual convention of the Association of Official Agricultural Chemists was called to order by the president, Mr. C. L. Penny, of Newark, Del., at 10 o'clock on the morning of November 16, at the George Washington University, Washington, D. C.

The following members and visitors were present during the convention:

MEMBERS AND VISITORS PRESENT.

Adams, Arthur B., U. S. Treasury Department, Washington, D. C.
Allen, William M., Department of Agriculture, Raleigh, N. C.
Ames, John W., Agricultural Experiment Station, Wooster, Ohio.
Averitt, Saxe Dabney, Agricultural Experiment Station, Lexington, Ky.

Barnard, H. E., State Chemist, Indianapolis, Ind.
Beal, W. H., U. S. Department of Agriculture, Washington, D. C.
Bell, James Munsie, U. S. Department of Agriculture, Washington, D. C.
Berkeley, William N., Food Laboratory, U. S. Department of Agriculture, Philadelphia, Pa.
Bigelow, W. D., U. S. Department of Agriculture, Washington, D. C.
Bonsteel, Jay Allan, U. S. Department of Agriculture, Washington, D. C.
Bowker, W. H., Bowker Fertilizer Company, Boston, Mass.
Boyle, Martin, U. S. Department of Agriculture, Washington, D. C.
Bradbury, Charles M., Department of Agriculture, Richmond, Va.
Brinton, Clement S., U. S. Department of Agriculture, Washington, D. C.
Burnet, Wallace C., U. S. Department of Agriculture, Washington, D. C.

Cameron, Frank K., U. S. Department of Agriculture, Washington, D. C.
Carpenter, F. B., Virginia-Carolina Chemical Company, Richmond, Va.
Carroll, John Sharkey, German Kali Works, Atlanta, Ga.
Cavanaugh, George W., Cornell University, Ithaca, N. Y.
Cavanaugh, Mrs. George W., Ithaca, N. Y.
Chace, Ed. MacKay, U. S. Department of Agriculture, Washington, D. C.
Chamberlain, Joseph S., U. S. Department of Agriculture, Washington, D. C.
Charron, Alphonse T., Experimental Farm, Ottawa, Canada.
Church, C. G., U. S. Department of Agriculture, Washington, D. C.
Claflin, Alan A., Littleton, Mass.
Claflin, Mabel N., Concord, Mass.
Cochran, C. B., Department of Agriculture, Westchester, Pa.

Cook, Frank C., U. S. Department of Agriculture, Washington, D. C.
Cory, Robert M., U. S. Department of Agriculture, Washington, D. C.
Crampton, Charles A., U. S. Treasury Department, Washington, D. C.
Crocker, Charles S., The American Agricultural Chemical Company, Philadelphia, Pa.

Davidson, Robert James, Agricultural Experiment Station, Blacksburg, Va.
Delaney, Charles R., Boston and Elliott streets, Baltimore, Md.
Doolittle, Roscoe E., Food Laboratory, U. S. Department of Agriculture, New York, N. Y.
Doyle, Aida M., U. S. Department of Agriculture, Washington, D. C.
Dubois, Wilbur L., U. S. Department of Agriculture, Washington, D. C.
Duncan, D. I., German Kali Works, New York, N. Y.

Eaton, Edward N., State Analyst, Chicago, Ill.

Failyer, Geo. H., U. S. Department of Agriculture, Washington, D. C.
Fields, John, Agricultural Experiment Station, Stillwater, Okla.
Fitz-Randolph, Raymond B., State Laboratory of Hygiene, Trenton, N. J.
Flint, Edward R., Agricultural Experiment Station, Lake City, Fla.
Foster, Arthur B., U. S. Patent Office, Washington, D. C.
Frear, William, State College, Pa.
French, D. M., Alexandria, Va.
Fuller, F. D., Department of Agriculture, Harrisburg, Pa.

Garner, Wightman W., U. S. Department of Agriculture, Washington, D. C.
Gascoyne, William J., 2741 North Charles street, Baltimore, Md.
Gladding, Thomas S., 55 Fulton street, New York, N. Y.
Goodrich, Charles E., U. S. Department of Agriculture, Washington, D. C.
Gore, H. C., U. S. Department of Agriculture, Washington, D. C.

Hand, William F., State Chemist, Agricultural College, Miss.
Harcourt, Robert, Ontario Agricultural College, Guelph, Canada.
Harcourt, Mrs. Robert, Ontario Agricultural College, Guelph, Canada.
Hardin, Mark Bernard, Agricultural Experiment Station, Clemson College, S. C.
Hare, Raleigh F., Agricultural Experiment Station, Mesilla Park, N. Mex.
Hargrove, Julian O., 1603 O street NW., Washington, D. C.
Harrison, Channing W., U. S. Department of Agriculture, Washington, D. C.
Hart, Edwin B., Agricultural Experiment Station, Geneva, N. Y.
Hartwell, Burt L., Agricultural Experiment Station, Kingston, R. I.
Haskins, Henri D., Hatch Experiment Station, Amherst, Mass.
Haywood, J. K., U. S. Department of Agriculture, Washington, D. C.
Herff, B. von, German Kali Works, New York, N. Y.
Hirsch, Rudolph, U. S. Department of Agriculture, Washington, D. C.
Hite, Bert H., Agricultural Experiment Station, Morgantown, W. Va.
Hoover, George W., U. S. Department of Agriculture, Washington, D. C.
Hopkins, Cyril G., Agricultural Experiment Station, Urbana, Ill.
Houghton, Harry W., U. S. Department of Agriculture, Washington, D. C.
Howard, Burton J., U. S. Department of Agriculture, Washington, D. C.
Hurt, Henry H., U. S. Department of Agriculture, Washington, D. C.
Huston, H. A., 562 Monadnock Building, Chicago, Ill.

Jones, Charles H., Agricultural Experiment Station, Burlington, Vt.

Kastle, Joseph H., Hygienic Laboratory, Washington, D. C.
Kebler, L. F., U. S. Department of Agriculture, Washington, D. C.
Keister, John T., U. S. Department of Agriculture, Washington, D. C.
Kenney, Frederick, Department of Health, New York, N. Y.
Kerr, Robert H., College Park, Md.
Kilgore, B. W., State Chemist, Raleigh, N. C.

Le Clerc, J. Arthur, U. S. Department of Agriculture, Washington, D. C.
Ladd, Edwin F., Agricultural Experiment Station, Fargo, N. Dak.
Langworthy, C. F., U. S. Department of Agriculture, Washington, D. C.
Lapham, Macy H., U. S. Department of Agriculture, Washington, D. C.
Law, Leroy M., U. S. Treasury Department, Washington, D. C.
Lawson, Huron W., U. S. Department of Agriculture, Washington, D. C.
Leach, Albert E., State Board of Health, Boston, Mass.
Leavens, George D., Coe-Mortimer Company, New York, N. Y.
Lipman, Jacob G., Agricultural Experiment Station, New Brunswick, N. J.
Livingston, Burton E., U. S. Department of Agriculture, Washington, D. C.
Loomis, Henry M., Department of Agriculture, Harrisburg, Pa.
Lounsbury, William C., U. S. Department of Agriculture, Washington, D. C.
Lynch, Robert L., Health Office, Washington, D. C.

McDonnell Henry B., Agricultural Experiment Station, College Park, Md.
McGill, A. M., Chemist to Canadian Government, Ottawa, Canada.
McGill, William, Hamilton, Ontario, Canada.
Magruder, E. W., Department of Agriculture, Richmond, Va.
Mason, Glen F., H. G. Heinz Company, Pittsburg, Pa.
Mewborne, Robert G., Kentucky Tobacco Product Company, Louisville, Ky.
Moore, C. C., U. S. Department of Agriculture, Washington, D. C.
Mooers, Charles A., Agricultural Experiment Station, Knoxville, Tenn.
Morgan, J. J., Agricultural Experiment Station, College Park, Md.
Morse, Fred W., Agricultural Experiment Station, Durham, N. H.
Munson, L. S., U. S. Department of Agriculture, Washington, D. C.

Nelson, Cyrus W., U. S. Department of Agriculture, Washington, D. C.
North, John, Eimer & Amend, New York, N. Y.

O'Connor, Charles P., Department of Health, New York, N. Y.

Patrick, George E., U. S. Department of Agriculture, Washington, D. C.
Patten, Andrew J., Agricultural Experiment Station, Agricultural College, Mich.
Patterson, H. J., Agricultural Experiment Station, College Park, Md.
Penny, Charles L., Agricultural Experiment Station, Newark, Del.
Porter, F. B., Swift & Co., Chicago, Ill.

Ragan, E. T., U. S. Department of Agriculture, Washington, D. C.
Reed, Herbert C., Stamford Manufacturing Company, Stamford, Conn.
Richardson, Mrs. W. D., Chicago, Ill.
Richardson, W. D., Swift & Co., Chicago, Ill.
Ross, B. B., State Chemist, Auburn, Ala.
Rose, R. E., State Chemist, Tallahassee, Fla.
Runyan, Elmer G., Inspector of Gas and Meters, Washington, D. C.

Sawyer, Ellen M., Boston, Mass.
Sawyer, Harris E., Felton & Son, Boston, Mass.
Schlesinger, Barthold E., Merrimac Chemical Company, Brookline, Mass.
Schreiber, J. H. A., U. S. Department of Agriculture, Washington, D. C.
Schreiner, Oswald, U. S. Department of Agriculture, Washington, D. C.
Schulz, Henry L., U. S. Department of Agriculture, Washington, D. C.
Scovell, M. A., Agricultural Experiment Station, Lexington, Ky.
Seidell, Atherton, U. S. Department of Agriculture, Washington, D. C.
Simons, Frank D., U. S. Treasury Department, Washington, D. C.
Sindall, Harry E., U. S. Department of Agriculture, Washington, D. C.
Skinner, W. W., U. S. Department of Agriculture, Washington, D. C.
Smith, B. H., Food Laboratory, U. S. Department of Agriculture, Boston, Mass.

Smith, Clinton D., Agricultural Experiment Station, Agricultural College, Mich.
Smith, Edwin, jr., Rockville, Md.
Smith, William B., U. S. Department of Agriculture, Washington, D. C.
Snyder, Harry, St. Anthony Park, Minn.
Stiles, George W., jr., U. S. Department of Agriculture, Washington, D. C.
Straughn, M. N., Agricultural Experiment Station, College Park, Md.
Street, John Phillips, Agricultural Experiment Station, New Brunswick, N. J.
Sullivan, Arthur L., U. S. Treasury Department, Washington, D. C.
Sullivan, Thomas V., U. S. Treasury Department, Washington, D. C.

Taber, Walter C., U. S. Department of Agriculture, Washington, D. C.
Teas, William H., Elk Tanning Company, Ridgway, Pa.
Tolman, L. M., U. S. Department of Agriculture, Washington, D. C.
Trescot, T. C., U. S. Department of Agriculture, Washington, D. C.

Van Slyke, Lucius L., Agricultural Experiment Station, Geneva, N. Y.
Veitch, F. P., U. S. Department of Agriculture, Washington, D. C.
Voorhees, Edward B., Agricultural Experiment Station, New Brunswick, N. J.

Wahl, Robert, Wahl-Henius Institute, Chicago, Ill.
Walker, Percy H., U. S. Department of Agriculture, Washington, D. C.
Warner, Harry J., U. S. Department of Agriculture, Washington, D. C.
Weber, F. C., U. S. Department of Agriculture, Washington, D. C.
Wetterstroem, Theo. D., Dairy and Food Commission, Cincinnati, Ohio.
Wheeler, H. J., Agricultural Experiment Station, Kingston, R. I.
White, H. C., Agricultural Experiment Station, Athens, Ga.
Wiley, H. W., U. S. Department of Agriculture, Washington, D. C.
Wiley, Raymond C., Agricultural Experiment Station, College Park, Md.
Wiley, Samuel W., American Agricultural Chemical Company, Baltimore, Md.
Williams, Charles B., Department of Agriculture, Raleigh, N. C.
Wilson, Clarence P., U. S. Department of Agriculture, Washington, D. C.
Winton, A. L., Agricultural Experiment Station, New Haven, Conn.
Withers, W. A., Agricultural Experiment Station, West Raleigh, N. C.
Woglum, Russell S., Agricultural Experiment Station, Raleigh, N. C.
Woods, Charles D., Agricultural Experiment Station, Orono, Me.

Yoder, P. A., Agricultural Experiment Station, Logan, Utah.
Yule, Miss L., Guelph, Canada.

The order of business was as follows:

ORDER OF BUSINESS.

The president's address.

Appointment of committees (committees on resolutions, on nominations, on amendments, and committees A, B, and C on recommendations).

Reports of referees:

1. Sugar. L. S. Munson.
2. Tannin. H. C. Reed.
3. Insecticides. B. H. Smith.
4. Foods and feeding stuffs. J. O. La Bach.
5. Food adulteration. W. D. Bigelow.
6. Dairy products. G. E. Patrick.
7. Soils. C. G. Hopkins.
8. Inorganic plant constituents. R. W. Thatcher.
9. Potash. G. S. Fraps.

10. Determination of nitrogen. F. W. Robison.
11. Separation of nitrogenous bodies:
    - Milk and cheese proteids. R. Harcourt.
    - Meat proteids. W. D. Bigelow.
    - Vegetable proteids. J. S. Chamberlain.
12. Phosphoric acid. E. W. Magruder.
13. Medicinal plants and drugs. L. F. Kebler.
14. Reports of special committees:
    - Food standards. William Frear.
    - Fertilizer legislation. H. W. Wiley.
    - Testing chemical reagents. L. F. Kebler.
    - Unification of terms for reporting analytical results. R. J. Davidson.
    - Unification of soil methods. L. L. Van Slyke.
    - Definition of plant food. H. W. Wiley.
15. Reports of committees A, B, and C.

APPOINTMENT OF COMMITTEES.

Committee on resolutions, Messrs. Hopkins, Ladd, and McGill.

Committee on nominations, Messrs. Frear, Kilgore, and Davidson.

Committee A, on recommendations of referees (phosphoric acid, potash, nitrogen, soils, ash, and insecticides), Messrs. Street, Snyder, McDonnell, H. B., Withers, and Hartwell.

Committee B, on recommendations of referees (dairy products, foods and feeding stuffs, sugar, tannin, and medicinal plants and drugs), Messrs. Van Slyke, Woods, Patrick, Jones, C. H., and Hart.

Committee C, on recommendations of referees (food adulteration), Messrs. Winton, Bigelow, Leach, Barnard, and McGill, A. M.

On motion a committee was appointed to invite the Secretary and Assistant Secretary of Agriculture to address the association, the president naming Messrs. Withers, Hardin, and Scovell.

Committee on amendments to the constitution: Messrs. Wheeler Ross, and Cavanaugh.

PRESIDENT'S ADDRESS.

Gentlemen of the Association of Official Agricultural Chemists:

In this your twenty-second annual meeting you come together under most favorable auspices. The need of your association is more widely recognized, your past work is more highly appreciated, and there is in prospect more for every active brain to do than ever before. We may at this season, I hope, be pardoned for a little self-complacency when we consider how great and good we are. Surely the gentleman who projected the organization and all who have since labored for its welfare may feel a just pride that it has grown to be what it is. To any one, however eminent, it is a privilege to be numbered among its members, and perhaps it is not in too bad taste to say that it has numbered and does number among its members some as expert in their specialty as any of their day. Of all whose offices or professional labors are within the scope of its constitution it is the duty to be active workers in its cause. Few men are too wise to learn in this school, and any such ought at least in charity to let their light shine. No man, however obscure, will fail to find here a warm welcome and a generous appreciation of whatever of real worth he may bring in a forum as fair and free from bias as any in the world. It is an honorable ambition to aim at discovery. A new idea embodied in a really useful method of analysis may be a widespread and lasting benefit.

Few are privileged to make brilliant discoveries in our field, as in all others, but every man ought to feel a longing to leave behind him some contribution to our stock of knowledge. Whether the gift be money or knowledge, they are ingrates who only take and never try to give. The busiest man of routine ought to do something to perfect his science and art, to improve the tools of his daily trade. There are probably few men of long experience so stupid as not to have learned something not generally known and well worth the telling. Some of my accomplished predecessors have wisely emphasized the need of hearty and general cooperation in the analytical work. This can not be too strongly urged. It must be remembered that while debate clears up obscurities and removes misunderstandings, it is originally the burette and the balance that teach, and in the combination of actual laboratory experience and conference with colleagues the surest advance may be made.

The growth of the association in numbers, its much greater growth in the technological field covered, and in its importance to the welfare of society have been repeatedly pointed out and are obvious to all who knew its earlier days. Planned at first to regulate the sale of a single commodity, it bids fair soon to control the exchange of almost every article of domestic consumption. Beyond assuring a dollar's worth for a dollar spent, it aims now at safeguarding human health and life. Every right-minded man whose privilege it is to work in such a cause must feel his responsibility. You, gentlemen of the association, are charged with a most weighty duty and one that should be met conscientiously. You may be asked to define or alter analytical procedures that may change valuations by immense sums of money. Nothing less than the spirit of absolute fairness that has always characterized your enactments will discharge this duty.

The association is largely made up of arbiters of questions in which they have no selfish interest. Obviously, partizan advocates should have no vote on such questions, but the floor has always been free to the advocates of any commercial or other interest. Gentlemen retained in such a cause are always welcome to state here any grievance they may suffer or to urge upon the association any course of action they may think proper. This would seem to be all that a liberal justice could concede. The practice sometimes followed by the representatives of commercial interests of soliciting through private communication the views of members to be expressed likewise through private communication is to be condemned. This is a place for free and untrammeled expression of opinion. If members have views at variance with the established methods of analysis, and many must necessarily have some such, they owe it to their colleagues to explain their views. The catechetical method has always been dangerous—in expert hands it is far better fitted to suppress than to elicit the truth. A private communication from members on such a matter and in such an interest is in the last degree unwise, not merely as tending to show want of harmony, but also because the receiver may make such use of the communication as he may think best—publishing, excerpting a part, or suppressing altogether. All commercial interests affected by the association's action are free to state their case here on the floor. If they choose in addition to this by letter or otherwise to present their views in advance of a meeting there could be no objection. But it seems clearly to be unwise on the part of members to commit themselves in advance or at any time, by private communication, on questions of that sort. It approaches too nearly a solicitation out of court, in which only one side appears.

Like almost everything else of healthy growth, the association has developed in conformity to its environment—the changing and increasing needs of the times. Its future no one will attempt to forecast, but it surely promises a continually wider and more beneficent usefulness. Many will recall the view expressed over a decade ago that it had about fulfilled its mission, for the work appointed it seemed finished. But, in fact, the end seems farther off now than ever. Every year, instead of bringing less for such an institution to do, brings more. The commodities subjected to official inspection are yearly increasing; the technological demands on analysts are greater now than ever before. The illustrious Wöhler is reported to have said: "I am the last man to know all chemistry." Analogously it must needs be a diversified and experienced analyst who knows all the official methods. The division of labor has been carried far. Probably some years ago a man knew as much about one subject of analysis as another—as much about phosphoric acid as about fat-extraction; and the same chemist served in turn as reporter and expert adviser on different questions. But now the subject-matter has expanded to such an extent that this is impracticable. We have long been recognizing a specialized fitness in our referees.

A most noteworthy change in the character of the official methods is that while they were formerly all quantitative, many of them now are concerned with purely qualitative tests. Ultimately these latter may verge upon the quantitative, for such has always been the rule of analytical development. As soon as we have answered the question "what" we seek to know "how much." But evidently at present a most important branch of official analysis is the purely qualitative. The use of optical tests by the microscope, the polariscope, the refractometer, and the spectroscope while not new is still widening the analyst's field.

The proceedings of the association are a store of exact experience in which the most learned may find much that is new and valuable. They furnish a mass of expert testimony the like of which I should not know where to look for, with the supreme merit all too rare in expert testimony, that it is fair. The witnesses for the most part are not retained by one side or the other. Their opinions may sometimes be in error but they are honest. Nearly every word is the testimony of an eyewitness. It is the experience of men with actual conditions unbiased by tradition or theory. I doubt if elsewhere any similar questions have been weighed by as many independent minds or by means of as thorough tests. If the shortcomings of the analytic art have been laid bare it has been a wholesome even though unwelcome revelation. Probably most men of the various sciences of precise measurement somewhat overrate each the precision of his own science, and greatly overrate that of alien sciences. They who compare their work with their own repetition of it often fail to distinguish between self-consistency and truth. While all truth is self-consistent, all self-consistency is not truth. The recluse investigator is too likely, figuratively speaking, to be geocentric rather than heliocentric. He never allows for his own variation; he measures everything but his own error. He lacks the light that other minds can always give. And a method of analysis has a subjective side as well as an objective; the human element enters in as well as the laws of matter. The practical question is not merely what might be under ideally defined conditions, but also what actually is under real conditions, human conditions, personal conditions, as well as those of temperature and reagents.

The weakness of academic criticisms, of which the works of Fresenius furnish a type, is that they are so largely controlled by the inventor's favoritism or the rival's prejudice. A system of analysis emanating from a single center is likely to be narrow and ill-adapted to diverse conditions; so, often a proposed method fails in everybody's hands except the discoverer's. Analysis rests on science, but it is none the less an art—an art not vouchsafed by the highest scientific insight, as witness the father of modern chemistry, John Dalton. They who practice are usually better qualified to judge within the scope of their practice than they who only teach, and a hundred men who work together will know manifold more than if each worked by himself.

Now, after a score of years of comparative work aimed chiefly at securing greater uniformity in analytical results it seems proper to inquire what progress has been made. The urgent need of reform before the day of the association is too well remembered by gentlemen long engaged in this work and too often impressed upon those who have more recently entered the field to call for comment now. In general, successive reporters and referees have professed themselves pleased with a visible progress, always, however, hoping for more. A comparison of the earlier figures with the more recent shows in the main a gratifying improvement. With the three great fertilizer constituents, for example, the variations in total phosphoric acid were less than one-half and those in potash less than one-fourth as great in 1904 as in 1886. It is to be regretted, however, that the comparison in the case of nitrogen by the Kjeldahl method, perhaps the most important of all, is less gratifying. If we may judge from cooperative analyses there seems to be, after seventeen years of comparative study, but little progress in the art of determining total nitrogen; or if at times progress, then certainly retrogression, for the average of extreme variations in 1887 seems to have been about 14.5 per cent and last year about 13 per cent as a mean of figures obtained for a number of different substances.

If I venture to speak on a special question that the accomplished referee and associate are far better qualified to discuss, it is only because I think its importance justifies me. A comparison of the cooperative analyses running through several years seems to show an extreme variation among different analysts for all substances of about 10 per cent. In other words, 100 pounds of nitrogen may be expected to be rated by some gentlemen as 95 and by others as 105 pounds. Hay seems to be the substance that makes the most difficulty, unfortunately for the agricultural investigators, since so much of experimental nitrogen work deals with the dried stalks and leaves of small plants. All that is said here on the Kjeldahl method, it may be well to state, excludes the troublesome question of nitrates; the nitrogen is in every case of "organic" origin. Experience during the last year or two with the unpublished results of cooperative nitrogen determinations seems to show the variation named, 10 per cent, to be about the proper expectation among a number of analysts. The cause of such variations some years ago was thought to be personal inexperience, carelessness, and the like, a cause eventually to be removed by better training, larger experience, and an improved personnel.

Many of the more experienced gentlemen of the association work rather in a supervisory capacity than in the way of actual manipulation, and this fact may indicate that some of the variation is due to insufficient practice on the part of the actual analysts. If so, that is nevertheless a poor consolation to those whose interests may be adversely affected; and certainly the high skill and ripe experience of gentlemen charged with supervision rather than with actual manipulation ought in some way to avail their laboratories to the end that more accurate work might be done. Studying the question objectively as from the outside, all that one can say is that samples sent to the best known laboratories show a surprising degree of variation in total nitrogen determinations; if a little extra care and supervision will change this, the fact can not be known too soon; if the cause is deeper and harder to remedy, then again the first step is to know the fact. The experience of the gentlemen in charge of laboratories, if not always that of the actual manipulators, is ample, and their reputations a guaranty of the best work obtainable, yet two such men, or perhaps more accurately the analysts under their official supervision, are likely to be at opposite ends of the line, one highest and one lowest, but in point of the known and unquestioned technical ability of the chiefs, as nearly equal as two men may be.

Now a study of these variations in nitrogen shows sometimes a tendency of a particular laboratory in one direction or the other, but often the analyst highest on one substance is simultaneously among the lowest on another. That this is not generally due to standard acids or to distillation is evident from the much greater concord obtained with certain substances than with others. Much of the variation in my opinion is chargeable to the vagaries of digestion.

The Kjeldahl method, perhaps the most novel and useful discovery in analytical chemistry of the last half century, is about coeval with this association, to some of whose members no small part of its development, or at least no small part of our knowledge about it, is due. Apparently simple, it is really full of pitfalls for the unwary and even for the experienced. That its difficulties are not always recognized is due to the uniformity of procedure coming from long practice, and uniformity of procedure, by making uniform errors, uniform deficits, and uniform excesses, tends to constancy of results. It is precisely this self-delusion that the cooperative work of this association is intended to remove, and that, too, quicker than can any other school; our shortcoming is in the small amount of this cooperative work and the scant heed paid to it after it is done and published.

Of the more prominent methods now in use this one is probably the most obscure as to the nature and completeness of its reactions. Sherman and others,[a] have recently shown the extraordinary variations caused by longer or shorter time of digestion as well as choice of reagents, and our proceedings bear abundant testimony to the same effect. The faint color change is about all that the analyst has as indication of complete digestion, and this is misleading, each different kind of substance behaving after its own peculiar fashion. This is apparent from the much greater uniformity obtaining at the hands of the same analysts with some substances than with others. Not infrequently a high nitrogen content is estimated more closely, judged by absolute not proportional difference in the figures, than a low one. In some substances the nitrogen may all be reduced to ammonia long before the yellow color has disappeared and in others it resists reduction for some time after the solution has become colorless. In addition to this, an improper disposition of the flame such that it strikes the dry walls of the flask must at times decompose some ammonium sulphate to free nitrogen. In fact, it might be well to consider whether the small amount of acid prescribed, 20 cc, does not facilitate this loss.

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[a] J. Amer. Chem. Soc., *26*: 367, 1469.

Now, I incline, without much hesitation, to charge a great part of these enormous and deplorable discrepancies to inherent and insufficiently recognized difficulties of analysis. That inadvertence, accident, and mistake all play their part is probable enough, but after allowance for these there remains an appalling amount of inaccuracy. I can not but think that this condition of affairs reflects the present state of the art.

Nitrogen, the most valuable of the three great agricultural elements, the only one we can grow, and the one that the experimenter is most concerned with, is, unfortunately, the hardest to measure exactly. Perversely enough, where the closest measure is needed we give the loosest. What these discrepancies mean commercially anyone may see—in a hundred dollars' worth of protein feed ten dollars' difference of opinion, or, if the truth be assumed to be near the mean, then sometimes five dollars too much and again five dollars too little, but probably without much chance of equitable compensation by the balancing of errors. In agricultural investigation it is rather worse, because the differences that selection or season give are so small that one-tenth makes an intolerable error. For example, certain gentlemen have been selecting corn for propagation with a view to increasing the protein content, and, after seven years of selection, apparently with great success. Now, assuming a uniform increase, four years of these seven would be required to annul the discrepancies between extreme analysts. In other words, if the corn grower had sent his first seed corn to a certain laboratory and that from his fourth crop to a certain other laboratory he might have learned that he was exactly where he had started, with no gain whatever as the result of four years of selective propagation. This is intolerable, but it is not exaggerated, for there was ground enough to say seven years out of seven instead of four out of seven. I have been interested in some experiments with leguminous plants. Now, I should be glad, if I might, to send all samples to any one of a number of laboratories, with full confidence in the reliability of the results for the purpose of comparison, but I should not dare to send certain samples to one laboratory and other samples to another laboratory. So much of the differences between samples, due to the causes in the field—causes that are the sole object of study—would be swallowed up in the discrepancies among different analysts that the comparison would be vitiated. The physiologist Bernstein says that the untrained muscular sense can guess a difference of 1 in 16, or 6 per cent, and the trained muscular sense 1 in 40. Then if the nitrogen in a bale of hay were separable and ponderable a farm laborer, by simply "hefting" it, could guess closer than we analyze.

All gentlemen may not agree with the above attempted statement of fact, but I regard it as simply a fact of observation. After a score of years of trying, it is not amiss to talk about what actually is instead of what might be. Whatever uniformity ideal conditions might secure, whatever many able and experienced gentlemen may be able to do, present conditions, in my opinion, have given us what I have described. I fear the association is weary, *ad nauseam*, of the comparison of mere analyses by different persons, and members have repeatedly said, and that long ago, that we must seek new worlds to conquer; that all had been done that could be done for uniformity in nitrogen, potash, and phosphoric acid determinations. I go as far as anyone in approving the enormous expansion of the association's field of labor, and I am glad to see the field extended to include the all-important question of agricultural availability. But I can not agree that the mere technological question of analysis shall now be left as finished work.

At the risk of seeming unscientific, perhaps puerile, I venture to suggest the value of permanent reference samples as a sort of guide or means of orientation. In the metric system the unit of length was based on the earth's quadrant and the unit of weight in turn upon a volume of water under the most precise definition that has ever been attempted, and thus, with the stars for a clock, primal standards of space, mass, and time were established, to remain unchanged so long as the world should last. And recently the electricians, abandoning a given column of mercury for the unit of resistance, defined their ohm in terms of the rational, or C. G. S., system. And what, now, is the result of it all? A failure. Not one of these definitions is valid to-day. The meter is not the exact fraction of the earth's quadrant, as intended, but a certain metallic yardstick, carefully copied and safeguarded; the kilogram is not a liter of water, but a certain platinum weight, and the ohm is not the exact C. G. S. unit, but the resistance of a certain coil of wire from which the theoretic ohm has already been found to differ appreciably. Thus in these widely different kinds of measurement, compared with which, in point of accuracy, our best analyses are hardly more than guesses, it was found almost at once that a concrete material example of a quantity is more certain, more precise, than any purely rational definition. Now, borrowing an idea from the iron and steel chemists, I can not but think that a similar principle applied to our work would afford a valuable step toward agreement. Let a sufficient number of carefully prepared samples—for example, of all concentrated feeds and of hay, and the like, hermetically sealed and guarded for years from change or loss by every means that the best information can suggest—be placed at the disposal of all chemists to analyze for the sake of comparison. I can not but think that this would be a most direct way of effecting what we all want—a closer agreement, the first and chief reason for the association's existence.

The surest way to measure our agreement, or our lack of it, is to apply a concrete material standard to our work, to abandon, at least, as a sole working guide, abstract verbal definition and to use tangible substance instead. In other words, like the physicists, for everyday use we might well drop the earth's quadrant that we can not measure twice alike and take up the metal yardstick that we can measure near enough. If there were a question of tuning two musical strings to unison, Professor Helmholtz might possibly, by determining their weight, length, and tension, attempt to judge how nearly they would accord; but a practical musician would sound them, and in the simple act would sum up six different measures and many calculations with square roots, and withal would come nearer the truth than Professor Helmholtz could possibly do by the laws of dynamics. So we can attune our discordant notes to unison most easily and certainly by a direct test. We may at once sum up in the final result the combined effect of all the known conditions, temperature, time, reagents, impurities, imperfect distillation, standard acid, indicators, and the rest, and besides these the most potent of all, the unknown and invisible reactions. A standard acid is a partial condition; standard reagents are partial. To define these conditions is important, indispensable, but not enough, for the net results may vary widely with all these known and recognized conditions in perfect agreement, since the unknown conditions of reaction outweigh all the rest, and these last may vary far beyond our power to detect. But a test by means of a uniform substance adds up all sources of error, from the balance to the burette, the unknown equally with the known, and gives their algebraic sum in the grand total. And if these grand totals can be made to agree, that is what we want—what we want first of all. Afterwards philosophic minds may ponder at leisure how it all came about and why it never came before.

Suppose we could get, now, all of the original substances, unchanged and absolutely intact, upon which so many hundreds of analyses have been made during the last twenty years, would they not have great value? Could we not settle finally many interesting points of doubt? Whereas, now, the best we can do is to throw over the past work and start in anew, only to repeat it all next year. The substances sent out at various times by referees have never been any permanent guide. Once analyzed, they were thrown away and their utility was lost, and some gentlemen were shocked to learn how far some others could get above the truth and others were disgusted that any tyro could fall so far below the truth. In the first year of comparison the mean variation between highest and lowest was a little over 14 per cent and in the seventeenth year about 13 per cent. Now, I believe that if certain chemists found their analyses, by repeated trials, to differ greatly from the most respectable average of their colleagues they would soon find some way to closer agreement. In correspondence with a number of friends, who have kindly cooperated for a different purpose than exploitation at this time, I find a general and perfectly natural desire to know what results others get, and sometimes it is frankly stated that it is for the purpose of checking up.

It may be objected that pure substances will furnish every means of rectification and comparison that could be desired. But as a matter of fact they do not. It is often no slight art to prepare such, and, furthermore, every distinct class of substance presents its own difficulties. A comparison by means of a pure salt would be useless for timothy hay or cotton-seed meal. In practice the analyst seldom works on a pure substance, but usually on troublesome and disturbing mixtures, and no means of comparison that ignores this feature can be reliable. All materials of comparison would have to be rigidly within their own respective classes, corn to be compared with corn, bran with bran, and the like.

One of the most urgent questions, affecting both equity in commercial dealings and the interests of agriculture, is that of the correct valuation of basic slag. This question has been carefully considered by the association at intervals during the last ten years and much interesting and profitable discussion has been called forth. Comparisons have been made of different methods of determining availability, and recently vegetation tests have been ordered. The association was for a time inclined to look on the question as a possible one for future decision, but not one demanded by the present state of trade. The small amount of slag offered on the American market was not regarded as warranting so important a change in methods as those proposed; and thus minded, five years ago the association declined to adopt provisionally a 2 per cent citric acid test. More recently reports from different parts of the country show a rapidly increasing trade in slag, and the association seems to be aware of the urgent need for action. The question presents the difficulties that special legislation always presents. Exceptions are usually embarrassing and dangerous, probably nowhere more so than in the official methods. In lieu, however, of a special analytical treatment for a single article, it has been proposed, and with much show of reason, to let the mechanical fineness and the total phosphoric acid indicate availability. The farmer's interests, which the association is first of all bound to protect, are thought to demand such measures as shall give him the benefit of this cheap and useful phosphate; and that, the sellers say, is commercially possible only when official analyses are made to show the true value of their product. There is no doubt that the gentlemen charged with fertilizer control appreciate the urgency and likewise the difficulty of the case. It is to be hoped a way may be devised speedily to give to agriculture the benefit which it seems to demand, without injustice to any trade interest and without danger of misleading valuations.

The institution of vegetation tests as bearing on the availability of supposed "plant food," is a new departure in the association's practice, though from the first the possible need of such a method was foreseen. I can not but regard what seems to be merely a subsidiary incident to the main question as a matter of great importance—of greater importance than the main question itself. An appeal from laboratory methods to the methods of nature is a momentous step. Unquestionably the association came into existence solely as an appraiser of values in trade; without trade it could have had no reason for being. Later it has been assuming the rôle of guardian of health and life, and has thereby multiplied its usefulness manifold. Thus far it stands as a quasi policeman or detective to secure to honest folk their due and to punish fraud. But now by studying to learn more of natural processes, or, in the classic words of the distinguished man whom it is our honor to call colleague, more of "how plants grow" and "how crops feed," the association enters upon a higher plane of usefulness. By helping to a better understanding of the deeply hidden mysteries of the soil it becomes a producer. Its mission will be not only to secure commercial truth and equity, but also to feed mankind.

Striving after exactitude in our analyses, we have examined freely every pertinent question of laboratory reaction and deportment. Venerable methods have had to go as soon as they were weighed and found wanting. But in the generally accepted basis of availability—a basis mainly conventional, reached perhaps only after considerable contention—we have been conservative, perhaps, to a fault. The unwisdom of many and radical changes no one questions, but we may well ask whether the association has not in this erred on the side of conservatism. It may have led a more peaceful life by settling once for all this most vexed and difficult question, but whether thus it has done the most good I do not presume to say. I think, however, a better understanding at least of the great laboratory methods of the soil, whether or not it might have changed valuations, would have been well. And this better understanding is only to be had in one way. Tyndall said, Nature always answers our questions truly, but she answers the questions we actually ask, not the questions we meant to ask, for in the language of experiment we do not always say what we mean. Now, the only intelligible form for such a question as this is vegetation experiments. I agree with those gentlemen who demur at accepting blindly the dictum of Paul Wagner. If we must walk by faith in this, why not in everything else? If we are to stand as an independent source of knowledge, if we are to speak as those who know, we must find out for ourselves.

Uniformity in the reports of analyses and in the mode of stating quantities, e. g., whether as oxids, according to unbroken custom hitherto, or as elements, may engage the attention of the association. This is a question of convenience rather than of equity, but certainly an important one. Ambiguity in terms ought not to be possible anywhere, and certainly not in science, but unfortunately it runs all through scientific literature. It is always hard to decide whether the simplicity and certainty of a new system will repay the loss caused by throwing over an old one. Without venturing an opinion on Phosphorus *v.* Phosphoric Acid and Calcium *v.* Lime, I quote the advice of Mallet expressed in his monograph on distinguishing the nitrogen of proteids,[a] namely, that in the matter of organic nitrogen compounds, under whatever name, the elemental nitrogen should invariably be given directly and then in addition its product by a factor also be stated for protein and the like. It has appeared recently that all stations have not been using the same protein factor in their publications. In a matter so little understood as the composition of these nitrogen bodies, it would seem to be wise to follow majority rule, even though at times it seem to be in error. Another source of misunderstanding arises from the varying practice of giving percentages, sometimes on the air-dry and again on the absolutely dry basis, without specific definition. As the reader may consult a table without seeing the explanatory text it seems to me that all tables should bear this explanation on their face to avoid a misunderstanding. If some conventional phraseology such as "air-dry protein" and "absolute protein" might be agreed upon it would perhaps give greater certainty.

REPORT ON SUGAR.

By L. S. Munson, *Referee.*

The sugar work done during the past year has been largely a continuation of the lines of investigation reported upon at last year's meeting. Upon the whole, results of the work are extremely gratifying. This is particularly true with the progress made upon methods for the determination of various reducing sugars in mixtures and of dextrose and levulose in the presence of sucrose, upon methods for molasses analysis, and upon the unification of reducing sugar methods.

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[a] U. S Dept. Agr., Bureau of Chemistry, Bul. 54. Analytical methods for distinguishing between nitrogen of proteids and nitrogen of simpler amids or amido-acids.

For several years past the writer's work for the association has been largely a study of reducing-sugar methods, with the idea of establishing a uniform method of manipulation and of determining the copper-sugar factors for the various reducing sugars. Mr. Browne, the associate referee on special analytical methods, in his work upon reducing sugars, has followed much the same plan, although the method used by him is not, in the writer's opinion the most satisfactory method for reducing sugar. In our study of reducing-sugar methods the ideal method was considered to be the one by which sucrose when present with the reducing sugar would have the minimum reducing action upon the copper. Experience soon demonstrated that an alkaline copper-tartrate solution, having satisfactory working qualities in other respects, would be acted upon by sucrose to a considerable extent. The alkaline tartrate solution, therefore, found to be the most satisfactory is what is known as Soxhlet's solution. This is prepared by dissolving together 50 grams pure caustic soda and 173 grams Rochelle salts, and completing the volume to 500 cc. The copper solution is prepared by dissolving 40 grams pure copper sulphate and making the volume up to 500 cc. This copper solution is somewhat stronger than the copper solution described by Soxhlet, for the reason to be stated further on. The method of manipulation is as follows:

Mix 25 cc each of alkaline tartrate solution and copper solution in a 400 cc Jena beaker and add 50 cc of sugar solution containing not more than 0.50 per cent of reducing sugar. Heat on a wire gauze over a Bunsen burner, so regulating the flame that the solution will come to a boil in four minutes. Boil exactly two minutes, keeping beaker covered throughout the heating with a cover glass, and filter at once without dilution. Wash the precipitate thoroughly, using care to remove completely the cuprous oxid from the sides and bottom of the beaker, and determine copper by one of the official methods.

In the determination of reducing sugars it is extremely important that details be followed exactly, and it is believed that the above method of manipulation combines both simplicity and accuracy if carefully followed. In order that the amount of copper in 25 cc of the copper solution may be sufficient to allow the determination of 250 mgs of dextrose it is necessary to increase the strength of the copper solution to 40 grams per 500 cc. This increase in no way influences the working qualities of the solution, although it does somewhat modify the copper-sugar ratio.

Throughout the investigation copper has been determined by direct weighing of the cuprous oxid, and this method has been found to give entirely satisfactory results. As a check upon this method, an adaptation of Low's volumetric method [a] has been used. The results obtained by this method are considered very reliable, and it has therefore been recommended that this method be made a provisional method of the association. The method is as follows:

LOW'S VOLUMETRIC METHOD (MODIFIED).

Standardization of thiosulphate solution.—Prepare a solution of sodium thiosulphate containing 19 grams of pure crystals to 1,000 cc. Weigh accurately about 0.2 gram of pure copper foil and place in a flask of 250 cc capacity. Dissolve by warming with 5 cc of a mixture of equal volumes of strong nitric acid and water. Dilute to 50 cc, boil to expel the red fumes, add 5 cc strong bromin water, and boil until the bromin is thoroughly expelled. Remove from the heat and add a slight excess of strong ammonia—7 cc is about the right amount. Again boil until the excess of ammonia is expelled, as shown by a change of color of the liquid, and a partial precipitation. Now add a slight excess of strong acetic acid (3 or 4 cc of 80 per cent acid) and boil for a minute. Cool to room temperature and add 10 cc of a solution of pure potassium iodid containing 300 grams of potassium iodid to 1,000 cc. Titrate at once with the thiosulphate solution until the brown tinge has become weak, then add sufficient starch liquor to produce a marked blue coloration. Continue the titration cautiously until the color due to free iodin has entirely vanished. The blue color changes toward the end to a faint lilac. If at this point the thiosulphate be added drop by drop and a little time be allowed for complete reaction after each addition there is no difficulty in determining the end point within a single drop. One cc of the thiosulphate solution will be found to correspond to about 0.005 gram of copper.

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[a] J. Amer. Chem. Soc., 1902, *24*: 1082.

Determination of copper.—After washing the precipitated cuprous oxid, cover the gooch with a watch glass and dissolve the oxid by means of 5 cc of warm nitric acid (1:1) poured under the watch glass with a pipette. Catch the filtrate in a flask of 250 cc capacity, wash watch glass and gooch free of copper, 50 cc of water will be sufficient. Boil to expel red fumes, add 5 cc of bromin water, boil off the bromin, and proceed exactly as in standardizing the thiosulphate.

RECOMMENDATIONS.

It is recommended—

(a) That the work as outlined in the report of the referee on sugars be continued until uniform methods are obtained for the various reducing sugars; that copper-sugar factors be determined for the various concentrations of the different reducing sugars and for various mixtures and proportions of sucrose and the reducing sugars.

(b) That the methods selected by the International Committee for Unifying Methods of Sugar Analysis, now provisional, be made official. (Proceedings of 1902, Bureau of Chemistry, Bul. 73, pp. 58, 59, par. 1 to 9 inclusive.)

(c) That method (a) for the determination of copper in the cuprous oxid precipitate, requiring reduction in hydrogen (Bureau of Chemistry, Bul. 46, p. 37) be dropped as an official method of this association.

(d) That methods (c) and (d) for the determination of copper in the cuprous oxid precipitate requiring the electric deposition of the metal (Bul. 46, p. 38) be dropped as official methods of this association.

(e) That Low's thiosulphate method for determining the copper in the cuprous oxid precipitate be substituted, as modified, for the volumetric permanganate method as a provisional method (Bul. 46, p. 38).

SPECIAL ANALYTICAL METHODS OF SUGAR ANALYSIS.

By C. A. BROWNE, JR., *Associate Referee.*

The work during the past year has been along the three lines indicated by the recommendations adopted at the last meeting, namely:

1. A study of a method for the analysis of simple mixtures of reducing sugars.
2. Further trials of a method for the determination of dextrose, levulose, and sucrose in mixtures.
3. An investigation concerning the influence of temperature upon the polarization of raw cane sugars.

The report on the first two studies named will be found in the Journal of the American Chemical Society;[a] the third investigation yielded the following results.

INFLUENCE OF TEMPERATURE UPON THE POLARIZATION OF RAW CANE SUGARS.

The influence of temperature upon the polarization of pure sucrose has been thoroughly investigated by Wiley,[b] Schönrock,[c] and others, and it is now generally conceded that the specific rotation of sucrose undergoes a perceptible decrease as the temperature of polarization increases. To correct for these variations in commercial work tables have been constructed by means of which all readings may be corrected to a constant temperature of polarization. The writer has attempted to use such a table in the polarization of cane sugars, and has come to the conclusion that while the table may be valuable in polarizing refined sugars it will not answer at all in the polarization of raw cane products. The reason for this is not difficult to find. We have in raw cane sugars, in addition to sucrose, appreciable amounts of the reducing sugars dextrose and levulose; now, while the specific rotation of dextrose is but very little affected by change in temperature, that of levulose is very decidedly influenced, more so than that of any other sugar, and what is of the most importance, the temperature influence upon levulose affects the polarization in directly the opposite way from the change in the rotation of sucrose. When polarizations are made at different temperatures these opposing influences may nearly neutralize one another, as in the case of the higher grade of raw sugars; in the case of the lower grade of products, however, the effect of the levulose may more than counterbalance the sucrose variation, with the result that the sugar polarizes considerably more at the higher temperature instead of lower, as is the case of refined sugars.

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[a] J. Amer. Chem. Soc., 1906, *28:* 439.

[b] Wiley, J. Am. Chem. Soc., *21:* 568.

[c] Schönrock, Zts. Ver. d. Zucker-Ind., *53:* 650.

To illustrate these points more clearly, the polarization of four raw sugars of different grades is given at 5° and 20° together with the polarization calculated from 5° to 20° according to the tables of sucrose corrections.

Observed and calculated polarizations of raw sugars at 5° and 20° C.

Grade of sugar.	Dextrose.	Levulose.	Polarization 5° C.	Polarization 20° C.	Calculated polarization 20° C. according to table of corrections.
	Per cent.	*Per cent.*	° *V.*	° *V.*	° *V.*
Fancy seconds	1.99	1.79	95.94	96.06	95.47
Choice seconds	2.41	2.37	89.78	89.87	89.38
Prime seconds	4.22	4.74	80.88	81.32	80.50
Common seconds	6.53	6.71	74.17	74.73	73.82

The results show that with low-grade sugars it is far better to do without the table of sucrose corrections, as in each of the above cases where such correction was made the error of reading was increased instead of diminished.

In addition to the foregoing, the associate referee has continued his work upon the identification and determination of the various organic bodies not sugar occurring in cane products, but this part of his report is not yet ready for publication.

Recommendations.

It is recommended—

(a) That the work upon the separation of sugars next year be submitted to collaborative trial.

(b) That the work upon the identification and determination of the various organic solids not sugar be continued.

REPORT ON MOLASSES ANALYSIS.

By Harris E. Sawyer, *Associate Referee.*

Two years ago the writer urged upon this association such an extension of its saccharimetric methods as would afford increased precision in the commercial analysis of low-grade cane molasses; and he suggested that polarization in a solution of one-half or one-fifth the "normal" concentration—a procedure sometimes adopted as a convenient but dubious procedure in the examination of very dark molasses—might be the best means of securing the desired increase in accuracy.[a] He has sought during his service as associate referee on molasses analysis chiefly to reach a definite conclusion on this point. In addition, however, he has given considerable attention to the determination of reducing sugars in molasses.

It will not be necessary to reproduce in this report the full evidence which the writer has obtained in his investigations of these points, since the details have been or will eventually be published in the Journal of the American Chemical Society. It is sufficient here to note the points investigated, to state the conclusions reached, and to make such recommendations as the latter seem to warrant.

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[a] U. S. Dept. of Agr., Bureau of Chemistry, Bul. 81, p. 175.

As was pointed out two years ago, the difficulties in the analysis of low-grade molasses by existing methods are due primarily to the necessity of employing excessive quantities of lead subacetate in removing the large proportions of coloring matter which such goods contain, and, secondarily, to the following causes:

(1) Undue concentration of the sugar solution and elevation of its polarization on account of the bulk of the lead precipitate.

(2) Change in the polarization of the solution on account of the action of the excess of lead, in basic solution, upon the rotatory power of levulose.

(3) Interference of a large excess of lead with the inversion of the sugar solution in determining sucrose by the method of Clerget.

(4) Impossibility of getting a solution of very dark molasses clear enough for accurate observation in the saccharimeter, even when an excess of lead subacetate is added.

It was shown to be possible to clarify a dilute solution of such molasses sufficiently for polarization with a reduced amount of lead reagent; and on this account the following advantages were claimed for the proposed procedure:

(1) The bulk of the lead precipitate and the error due thereto are materially reduced.

(2) The amount of lead passing into the sugar solution is so slight that the alteration in the rotatory power of levulose, referred to above, is done away with; and, furthermore, the reduction in this amount of lead facilitates inversion.

It was recognized, however, that since the observed polarizations of fifth-normal molasses solutions must be multiplied by five in order to obtain the true polarizations of the materials, the errors affecting the latter values will be five times as large as those affecting the former; and while it was clear that the actual error of an observed polarization on a fifth-normal solution of any dark molasses must be materially smaller than the error of a polarization on a normal solution of the same material, it was questionable whether the former error, when multiplied by five, might not equal or exceed the latter. In order to settle this question definitely it was necessary to investigate the following points:

(1) The effect of inaccuracies in weighing and measuring upon the probable errors of results obtained by polarizing fifth-normal and normal solutions.

(2) The relative probability of errors in the two procedures arising from the use of too much or too basic lead acetate solution.

(3) The possible magnitude of such errors as might arise from alterations of the rotatory power of the sugars of molasses, due to polarization in solutions of materially reduced concentration.

(4) The probable errors of polarization, as determined by the construction and illumination of the saccharimeter and by the carefulness and capability of the observer.

In a discussion of these points already published [a] it has been shown that such errors as may arise in weighing and measuring are likely to favor polarization in the fifth-normal solution. With regard to the several errors due to lead it has been found:

(1) That the plus error in the direct polarization, due to the bulk of the lead precipitate, amounts to about 0.05°–0.06° V. after multiplying the observed polarization by five, in routine analyses of dark molasses in solutions of fifth-normal strength. The corresponding error in the observed direct polarization of a solution of normal concentration is likely to be not less than 1.0° V.

(2) The elevation of the direct polarization of cane molasses due to the action of lead subacetate on the rotatory power of levulose, discovered by Gill and discussed by Spencer, Edson, and Pellet, may amount to several Ventzke degrees in a solution of normal strength unless the latter be acidified previous to polarization; and Pellet has claimed that with dark molasses, calling for the use of an excess of lead in decolorization, the polarization is left abnormally high, even after this acidification. In polarizing solutions of fifth-normal

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[a] Sawyer, The commercial analysis of cane molasses, J. Am. Chem. Soc., 1905, *27:* 691.

strength the writer has rarely found any sign of this elevation, even when the solutions had not been acidified.

(3) In a molasses solution made up and clarified at the normal concentration, about 13 per cent of the hydrochloric acid added for inversion was precipitated by the excess of lead present in the solution. In a fifth-normal solution of the same material, similarly treated, only 0.8 per cent of the acid was precipitated.

It was found that the probability of error in polarization, due to alterations in rotatory power of the sugars on account of diminution in the concentration of their solutions, was very slight. The maximum error from this source should not exceed 0.2° after multiplication by five.

The probable magnitude and effect of errors in the graduation and illumination of the saccharimeter have been studied with much care, and it is believed that the mean error introduced in a polarization from this source will hardly exceed ±0.3° after multiplication by five. The observation error affecting polarizations of light colored fifth-normal solutions should not exceed 0.2° V. after multiplication. The corresponding error obtained in working with the darker normal solutions will depend very much upon their intensity of color and on the weariness of the observer's eye. In the writer's experience it has rarely been less than ±1.0° V.

Summing up, it will appear that the direct polarization of a "normal" solution of dark molasses which has been clarified with an excess of lead subacetate will be affected by a plus error of at least 1.0° V., due to the bulk of the lead precipitate, by a further plus error of indefinite magnitude, due to the effect of the lead reagent on the levulose of the molasses and by an observation error which will amount on the average to about ±1.0° V. On the other hand, the polarization of a fifth-normal solution will be affected by a "bulk of precipitate" error amounting to less than 0.1°, a levulose error so small as to be negligible, a plus error due to changed rotatory powers in dilute solutions amounting to about 0.2°, and a total error due to irregularities in graduation, illumination, and observation amounting to about ±0.4° or ±0.5°. Furthermore, the inversion of the stronger solution is much more liable to retardation than that of the weaker, and the ease and comfort of the observer are promoted greatly by use of the weaker and paler solution for polarization. It therefore seems to the writer that the advocated procedure is a distinct advance in the direction of precision, and that it is worthy of recommendation and adoption.

The factor which is used as a divisor in the Clerget equation demands further study in connection with the polarization of fifth-normal solutions. The writer has found that the constant 142 seems to give more concordant results than any other, and he is using that value provisionally. But he hopes that further information may be obtained upon this point.

In addition to the writer's work upon the optical side of molasses analysis, he has undertaken some studies of the methods for determining the reducing sugars. In this connection three questions have appealed to him as demanding solution:

(1) Whether clarification with lead subacetate should precede the determination of reducing sugars.

(2) How best to remove the excess of lead from the clarified sugar solution, previous to the treatment with Fehling's solution.

(3) How to adapt the somewhat cumbersome Herzfeld-Hiller-Meissl method of gravimetric determination to the demands of routine work in a commercial laboratory.

The writer is strongly of the opinion that clarification with a minimum quantity of lead subacetate is necessary previous to making a reducing sugar determination on a molasses sample. Whether or not it be true, as Pellet has claimed, that an excess of basic acetate sometimes precipitates a part of the reducing sugars, the writer has not been able to obtain any evidence that such precipitation takes place in dilute solutions when small amounts of acetate are employed. The bodies which are thrown down under the latter conditions undeniably possess copper reducing power; but, as yet, the writer has not been able to find that they give any distinctly characteristic reaction of the reducing sugars, such as the formation of glucosazone. In sugarhouse work it may be legitimate to omit clarification and to figure these bodies as sugars on the basis of their reducing power. When, however, an accurate determination of reducing *sugar* is wanted they certainly ought to be removed.

The present methods of the association recommend the removal of the excess of lead from a clarified sugar solution previous to the determination of reducing sugars by the addition of sodic carbonate. It seems advantageous, as the writer has already shown elsewhere, to precipitate the lead as oxalate rather than as carbonate.[a]

A simplified procedure for determining the reducing sugars of molasses gravimetrically will be published as soon as the work of the associate referee on chemical methods has progressed a little further.

RECOMMENDATIONS.

The associate referee on methods of molasses analysis respectfully submits the following recommendations:

(1) That when the color of a molasses is so deep as to make difficult the decolorization of a "normal solution" to the extent necessary for accurate polarization, it should be made permissible—using proper precautions—to employ solutions of one-half or one-fifth the recognized normal concentration, and to obtain the actual polarization of the sample by multiplying the observed results by 2 or by 5.

(2) That the present direction of the official method, "With molasses and massecuites add sufficient acetic acid to convert the (lead) subacetate into the neutral acetate," be so changed as to indicate that the addition of acid should be made to the *clarified filtrate intended for the direct polarization* and not to the basic acetate solution nor to the mixture of molasses and lead reagent previous to filtration.

(3) That the use of boneblack, condemned by the international commission some years ago and now made unnecessary by the polarization in weaker solutions, be discarded.

(4) That the association adopt, provisionally, the use of potassium oxalate as a reagent for precipitating the excess of lead from clarified sugar solutions previous to subjecting them to the determination of reducing sugars.

(5) That such a portion of the paragraph on p. 39, Bul. 46, revised edition of 1899, as relates to the preparation of molasses and massecuite solutions for polarization, be changed to read substantially as follows (following the words "precipitable matter" in line 9):

> With molasses and massecuites, the employment, for clarification, of excessive quantities of the lead reagent is to be avoided. In case that 5 cc of standard lead subacetate solution fails to clarify solutions of these materials, containing the normal weight in 100 cc, sufficiently for accurate polarization, it is advisable to make the solutions up to 200 cc or even to 500 cc, and to obtain the actual polarizations of the samples by multiplying the observed polarizations by 2 or by 5.[b]

The portion of the filtrate employed for the direct polarization should be made faintly but distinctly acid to litmus paper, shortly before polarization, by the addition of a minimum amount of glacial acetic acid.

Furthermore, it is recommended that the paragraph beginning on line 16, p. 39, Bul. 46, and relating to the temperature of polarization be extended substantially as follows:

> When solutions of half-normal or fifth-normal concentration are used for polarization, the deviation of the zero point of the saccharimeter should be established by at least five settings and readings—preferably with the polariscope tube in place, empty, but fitted with its cover glasses[c]—and at least five settings and readings should be made for each polarization. In every case the mean observed polarization should be corrected before multiplication for the deviation of the zero point.

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[a] Sawyer, Potassium oxalate as a lead precipitant in sugar analysis, J. Am. Chem. Soc., 1904: *26:* 1631.

[b] The darkest third molasses, when its normal weight is diluted to the volume of 500 cc, ought not require more than 12 to 13 cc of standard lead subacetate for satisfactory decolorization.

[c] Sawyer, The commercial analysis of cane molasses, J. Amer. Chem. Soc., 1905, *27:* 704.

(6) With regard to next year's work upon molasses analysis, it is recommended that further study be made of the choice of a constant or variable factor for employment in the Clerget equation, and that a table of logarithmic factors be prepared for use with the new modification of the Soxhlet solution in computing the percentage of reducing sugars.

A UNIFORM METHOD FOR THE DETERMINATION OF REDUCING SUGARS.

By Percy H. Walker.

The tables of Allihn for dextrose and of Meissl for invert sugar being based upon the use of different solutions and somewhat different manipulation introduce unnecessary confusion in work on reducing sugars. At the suggestion of Mr. L. S. Munson the writer undertook to test a modification of the existing methods with a view to using one method of procedure for the determination of both dextrose and invert sugar.

Solutions used.—The alkaline tartrate solution used is the Soxhlet solution, 50 grams of sodium hydroxid and 173 grams of Rochelle salt dissolved in water and diluted to 500 cc. The copper sulphate solution is made by dissolving 40 grams of crystallized copper sulphate in water and diluting to 500 cc.

Determination.—Twenty-five cc of alkaline tartrate solution and 25 cc of copper sulphate solution are mixed in a 400 cc Jena or Nonsol beaker, the sugar solution added, and sufficient water to bring the volume of liquid in the beaker to 100 cc. Heat the beaker with a flame so regulated that boiling begins in four minutes, boil two minutes, filter at once, without diluting, through a well-prepared gooch. After filtering it is a good plan to return the filtrate to the beaker and again run through the gooch. This plan gives almost always perfectly clear filtrates and better duplicates than when one filtration only is made. Wash and dry in the usual manner and weigh the cuprous oxid. In one series the cuprous oxid was dissolved and the copper determined by the iodid volumetric method. The agreement in the copper determinations by these two methods was excellent. Pure dextrose was prepared by repeated crystallization from hot alcohol and finally drying over sulphuric acid. A moisture determination showed that the final product was dry. Of this purified dextrose weighed amounts were taken from 10 mg to 250 mg, in all 25 points within this range. Most of these points were determined by averaging three closely agreeing results; in no case was a value taken that represented less than two closely agreeing results.

For the invert sugar some pure sucrose prepared by the method of the International Committee on Unifying Methods of Sugar Analysis was made. The amount of invert sugar formed was taken to be $\frac{20}{19}$ the weight of the sucrose used. All flasks and pipettes used were carefully calibrated. Inversion was accomplished as follows:

Determined and estimated amounts of copper corresponding to different weights of dextrose and invert sugar.

Weight of sugar.	Dextrose.		Invert sugar.		Weight of sugar.	Dextrose.		Invert sugar.	
	Copper found.	Copper estimated.	Copper found.	Copper estimated.		Copper found.	Copper estimated.	Copper found.	Copper estimated.
Mgs.	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*
10	21.0	21.0	20.6	20.6	140	275.3	275.4	268.3	268.5
20	41.6	41.7	40.1	40.0	150	292.9	293.5	286.7	286.3
30	62.7	62.6	59.2	59.5	160	312.8	312.0	303.4	303.6
40	83.2	82.9	79.5	79.2	170	329.4	329.6	320.7	320.7
50	102.6	102.8	98.4	98.8	180	346.8	346.9	338.1	338.1
60	122.9	122.7	118.8	118.1	190	364.5	364.1	355.3	355.5
70	142.5	142.4	136.2	137.0	200	380.6	381.3	373.3	372.5
80	161.8	161.9	156.9	156.1	210	399.5	399.0	388.0	388.6
90	181.5	181.6	174.5	175.6	220	416.3	416.1	405.0	405.1
100	201.6	200.7	196.4	195.6	230	432.2	432.5	422.3	421.7
110	218.1	219.4	215.1	214.6	240	449.4	449.3	437.1	437.6
120	239.7	238.9	231.6	232.2	250	466.0	466.0	453.8	453.8
130	257.9	257.7	250.6	250.3					

The sucrose was weighed and transferred to a 100 cc flask using 70 cc of water, 4 cc of half normal hydrochloric acid was added, the flask placed on steam table and left there for thirty minutes, removed, cooled rapidly, 10 cc of fifth normal sodium hydroxid added, filled to mark and mixed. Aliquot parts of solutions made in this manner containing invert sugar ranging from 10 to 250 mg were treated exactly as the dextrose was treated. The 25 points determined in this series were also in the main the average of three, and never less than two, closely agreeing results.

The weights of copper found for the different weights of the sugars used are given in the table. Since each of these values may be affected by an error of several tenths of a milligram it was thought better on settling on final points from which a complete table is to be calculated to distribute these errors. Alternate values were averaged, and these averages then averaged with the determined values. The values thus calculated are shown in the third and fifth columns.

REPORT ON INSECTICIDES, FUNGICIDES, AND DISINFECTANTS.

By Bernard H. Smith, *Referee.*

In this year's work on insecticides, fungicides, and disinfectants the suggestions made in the recommendations of the last report have been followed, including comparative analyses upon samples of Paris green, London purple, tobacco extract, soda lye, sulphur dip, formaldehyde, chlorid of lime, and a phenolic disinfectant.

In the discussion following the report of last year, attention was called to the fact that formaldehyde as sold commercially was practically never of 40 per cent strength, and complaints from certain sections indicated that it was more or less variable in character. It was also stated that much of the bleaching powder on the market was inferior in quality. Acting upon these suggestions the referee has done some work along these lines. In addition to the usual analytical routine presented under the heading "Formaldehyde" there is given a summary of an investigation made during the year to determine the strength of the article as sold in different parts of the United States, while a supplementary paper gives some data showing the rapidity with which bleaching powder loses its available chlorin upon standing, largely due to chemical changes within the product itself.

Paris Green.

The work done upon Paris green was to further test the two modifications of the Avery-Beans method for determining total arsenious oxid which were last year recommended as optional official methods,[a] being methods 1 and 4 of those tried last year. The method there designated as 4 is Method 2 of the following table. The amount of the sample taken, however, for Method 1 was changed from 0.4 to 1 gram because the percentage of soluble arsenious oxid obtained varies slightly with the amount of sodium acetate used, as was suggested last year, and by taking 1 gram of the Paris green, the results are comparable with the original method. This made necessary a change in the manipulation in order to avoid too high a reading in the titration. The referee in directions sent out suggested boiling with sodium acetate in a 50 cc flask, making to mark, and filtering through a dry Gooch, determining soluble arsenious oxid in the filtrate; then dissolving the residue with hydrochloric acid into a 50 cc flask and titrating 10 cc as usual.

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 90, pp. 96, 97.

TABLE I.—*Paris green.*

Analyst.	Total arsenious oxid.	
	Method 1.	Method 2.[a]
	Per cent.	*Per cent.*
R. J. Davidson and W. B. Ellett, Blacksburg, Va.	56.62 56.87 56.74	56.66 56.48 56.47
R. W. Thatcher, Pullman, Wash.	56.48 56.26	56.19 56.25
W. R. Bloor, Pullman, Wash.	56.67 56.51	56.15 56.20
F. S. Shiver, Clemson College, S. C.	56.50	56.08
E. R. Flint, Lake City, Fla.	....	56.80
B. H. Smith, Bureau of Chemistry	56.63 56.55	56.47 56.39

[a] Method 4 of the 1904 report.

COMMENTS OF ANALYSTS.

R. W. Thatcher: In Method 1 the filtration through a dry Gooch was found impracticable and the titration of an aliquot of the filtrate undesirable because of the small amount of arsenious oxid in solution, hence the entire mixture after boiling with sodium acetate was transferred to a Gooch and filtered and washed thoroughly, the entire filtrate being titrated for soluble arsenious oxid. The insoluble residue was then dissolved in hydrochloric acid, made up to volume and an aliquot titrated for combined arsenious oxid.

F. S. Shiver: The results seemed to vary somewhat with the time the material was allowed to stand after treatment with hydrochloric acid. In both methods the longer the material stood the higher the results were.

DISCUSSION.

Mr. Thatcher's method of procedure is shorter and easier of execution than that suggested by the referee. The latter can see no reason for a variation such as mentioned by Mr. Shiver.

LONDON PURPLE.

The methods used for London purple were the same as in previous years, being found in Circular No. 10, Revised, of the Bureau of Chemistry with the exception that a suggestion [a] made by Mr. Davidson for the elimination of a portion of the coloring matter was incorporated. This modification has more recently been restated by the author as follows:

DAVIDSON'S MODIFICATION.

Total arsenious oxid.

Place two grams of London purple in a beaker and dissolve in about 80 cc of water and 20 cc of concentrated hydrochloric acid at a temperature of 80°. Cool and add sodium carbonate in slight excess, transfer to a 250 cc flask and bring to the mark; shake and filter through a dry filter into a dry beaker; acidify 50 cc with hydrochloric acid and add sodium bicarbonate, titrating with iodin as usual.

Total arsenic acid.

Acidify 50 cc of the solution prepared as described under total arsenious oxid, with hydrochloric acid, add 25 cc of concentrated hydrochloric acid and three grams of potassium iodid. Then proceed as directed under this determination in Circular 10, Revised, Bureau of Chemistry, page 4.

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 81, p. 199.

TABLE II.—*London purple.*

Analyst.	Total arsenious oxid.	Total arsenic oxid.	Soluble arsenious oxid.	Soluble arsenic oxid.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
F. S. Shiver, Clemson College, S. C	22.66	....	14.02	3.07
E. R. Flint, Lake City, Fla	22.87	19.67	11.39	....
W. R. Bloor, Pullman, Wash	21.99	20.19	13.02	2.79
	21.87	20.10	13.06	2.30
	....	....	....	2.60
J. H. Horton, Fayetteville, Ark	22.57	21.26	13.86	....
	22.72	....	14.36	....
	22.87	....	....	....
R. J. Davidson and W. B. Ellett, Blacksburg, Va	22.31	16.21	13.73	6.50
	22.46	16.26	13.61	6.27
B. H. Smith, Bureau of Chemistry	21.87	19.80	13.62	2.46
	22.17	20.42	13.62	2.60

DISCUSSION.

The results upon total arsenious and arsenic oxid are very satisfactory. Two analysts reported difficulty with the soluble arsenic oxid determination, but altogether the results are decidedly better than last year.

TOBACCO EXTRACT.

The nicotin results received on the samples of tobacco extract sent out were but three in number; and as these varied considerably, they are not given, because the discrepancies are believed to be due more to the lack of uniformity of the sample, which contained solid matter in suspension, than to faulty methods of analysis.

SODA LYE.

The methods used for the examination of soda lye are given in Circular No. 10, Revised, of the Bureau of Chemistry. Method 1 consists in treating the lye in dilute solution with barium chlorid, which precipitates the CO_2 of the carbonate as an equivalent of barium carbonate, while the equivalent proportion of caustic alkali remains in solution as barium hydroxid and is titrated with acid. Method 2 consists of titrating with potassium bisulphate, using methyl orange and phenolphthalein as indicators.

TABLE III.—*Soda lye.*

Analyst.	Method 1.		Method 2.	
	Sodium hydroxid.	Sodium carbonate.	Sodium hydroxid.	Sodium carbonate.
J. H. Norton, Fayetteville, Ark	73.75	4.80	73.84	2.39
	73.75	4.80		
	73.75	4.80		
E. R. Flint, Lake City, Fla	74.37	3.28	74.37	2.54
B. H. Smith, Bureau of Chemistry	73.85	3.64	73.63	3.08

DISCUSSION.

These methods, as in other trials, give fairly uniform results, but the work reported upon this sample is so limited that no recommendation will be made.

SULPHUR DIP.

As was pointed out in a paper submitted last year by the associate referee, Mr. S. Avery,[a] a large number of sulphur dips, consisting principally of calcium polysulphids, is now being placed upon the market. Their value depends upon the amount of sulphur in solution, and the method sent out with a sample this year was that suggested in the paper referred to, which consists essentially of oxidizing the sulphur compounds to sulphates (by means of hydrogen peroxid), which are subsequently precipitated by barium chlorid.

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[a] U. S. Dept. Agr., Bul. 90, p. 105.

TABLE IV.—*Sulphur dip.*

Analyst.	Month of analysis.	Weight of sulphur.	Sulphur by weight.
	1905.	*Grams per cc.*	*Per cent.*
R. W. Thatcher, Pullman, Wash	January	0.28614 .28556 .28592	22.66 22.61 22.65
B. H. Smith, Bureau of Chemistry	do	.2794 .2808	22.18 22.28
J. H. Norton, Fayetteville, Ark	April	.2661 .2662	21.07 21.08
E. R. Flint, Lake City, Fla	October	.2556	20.23

COMMENTS OF ANALYST.

R. W. Thatcher: Both the hydrogen peroxid and sodium hydrate used contained sulphur; hence all reagents were carefully measured out for use, blank determinations were run, and the weight of barium sulphate found deducted from the total obtained in the above determinations. Two blank determinations with all reagents gave 0.02440 gram and 0.0249 gram of barium sulphate, respectively, and a single determination omitting the hydrogen peroxid gave 0.0182 gram. With these precautions the method seems to be entirely satisfactory.

DISCUSSION.

The low results obtained by Mr. Flint could be accounted for by the fact that his analysis was made several months after the others and sulphur dips of this strength continuously deposit sulphur. In the oxidation after the saturated soda and the hydrogen peroxid have been added, analysts at the Bureau of Chemistry have obtained higher and more uniform results by not heating more than a half hour; the time, however, should not be made much less than this, for then the oxidation would not be complete.[a] Hydrogen peroxid nearly always contains appreciable amounts of sulphates, and sodium hydrate is generally anything but chemically pure. As pointed out by Mr. Thatcher, a blank on the reagents used is essential.

On the whole the method is very satisfactory and is a great improvement over the other applicable methods.

FORMALDEHYDE.

The methods used in analyzing the sample of formaldehyde were two of those previously compared, the hydrogen peroxid method and the potassium cyanid method.[b] The former was sent out as previously used,[c] but during the past year this method has been quite thoroughly studied and probable sources of error pointed out which explain why occasionally analysts have failed to obtain concordant results. Fresenius and Grünhut[d] early in the year called attention to the following interesting facts regarding this method:

(1) When the formaldehyde is added to the sodium hydroxid solution there is danger of part of the formaldehyde acting on the hydroxid, according to the equation $2HCHO+NaOH=HCOONa+CH_3OH$, before the peroxid is added, so that two equivalents of formaldehyde correspond to one equivalent of sodium hydroxid instead of the ratio being 1:1, as required by the Blank and Finkenbeiner method. (The equation followed in this method is either

$$HCHO+NaOH+H_2O_2=HCOONa+2H_2O$$

or

$$2HCHO+2NaOH+H_2O_2=2HCOONa+2H_2O+H_3.)$$

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[a] J. Amer. Chem. Soc., 1905, *27:* 244.

[b] U. S. Dept. Agr., Bureau of Chemistry, Bul. 81, p. 204.

[c] U. S. Dept. Agr., Bureau of Chemistry, Circular 10, Revised.

[d] Zts. anal. Chem., 1905, *44:* 16.

(2) Low and varying results are obtained if the flask is cooled during the time that the peroxid is acting on the formaldehyde.

In accordance with the first suggestion, if any pause is made in the procedure of the analysis between the adding of the formaldehyde and the hydrogen peroxid the result will be too low. If, on the contrary, the addition of the hydrogen peroxid begins immediately after the addition of the formaldehyde to the soda and is added fairly rapidly, the results obtained will be comparable and close to the truth. To obviate this source of error the authors referred to suggested the addition of 5 cc of hydrogen peroxid to the soda before the addition of the formaldehyde in order to prevent the first reaction taking place. In an article[a] recently published by Mr. J. K. Haywood and the referee upon the Blank and Finkenbeiner method the results of a trial of the latter suggestion are given, which show that when but 5 cc of peroxid are previously added it is used up almost immediately, and then, in the warm solution, the reaction first referred to begins to take place. We therefore now add the whole 50 cc of hydrogen peroxid to the soda before the addition of the formaldehyde, the details of the manipulation being as follows:

Measure out 50 cc of normal sodium hydroxid in a small Erlenmeyer flask (of 500 cc capacity) and add 50 cc of pure 3 per cent hydrogen peroxid. Now add from a pipette 3 cc of the formaldehyde solution under examination (the specific gravity of which has been previously determined), allowing the point of the pipette to almost reach the liquid in the flask. Place a funnel in the neck of the flask and put on the steam bath for 5 minutes, shaking occasionally during this time. Remove from the steam bath, wash the funnel with distilled water, cool the flask down to about room temperature, and titrate the excess of sodium hydroxid with normal acid, using litmus as indicator.

This cooling of the flask before titration with acid was found necessary in order to get a sharp end-reaction with the litmus. From the volume of formaldehyde used and the specific gravity the percentage by weight of formaldehyde can be determined.

The results reported in the table below, as has been intimated, were obtained by using the method in its original form, except that 15 minutes were allowed for the oxidation:

Table V.—*Formaldehyde.*

Analyst.	Method 1. (Hydrogen peroxid.)	Method 2. (Potassium cyanid.)
	Per cent.	*Per cent.*
W. R. Bloor, Pullman, Wash	31.98 31.28	31.32 31.43
R. A. Lichtenthaeler, Lake City, Fla	32.80	....
B. H. Smith, Bureau of Chemistry	32.40 32.29	32.42
J. H. Norton, Fayetteville, Ark	....	31.64 31.64 32.77

DISCUSSION.

The results are few in number and are not as close together as those given in the last report. The referee believes that if the revised hydrogen peroxid method just described were used, much closer agreement would be obtained.

The potassium cyanid method was last year recommended as an official method for use upon dilute solutions. As but two results are reported and these do not closely agree, the referee does not feel justified in making the recommendation for the second time, but would suggest that the next referee give the method a further trial.

COMPOSITION OF COMMERCIAL FORMALDEHYDE.

To determine the strength of the commercial article a number of samples of formaldehyde have been obtained by the referee during the past few months from different parts of the United States and subjected to analysis. The larger part of these samples was purchased directly for the Bureau of Chemistry in the open market, but the Ohio samples are an exception, having been forwarded by the State dairy commissioner. The results of the analyses and the source of the samples are given in the following table:

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[a] J. Amer. Chem. Soc., 1905, *27:* 1183.

Table VI.—*Analyses showing percentage strength of commercial formaldehyde in samples obtained in 1905.*

No.	Formaldehyde.	Place of manufacture.	Place of purchase.	Remarks.
	Per cent.			
1	37.90	Michigan	Atlanta, Ga	Slightly cloudy.
2	35.95	Missouri	do	
3	37.45	Unknown	do	
4	37.62	Michigan	Fayetteville, Ark	
5	37.81	Unknown	do	
6	37.81	do	Amherst, Mass	
7	37.20	do	Northampton, Mass	
8	32.45	Germany	do	
9	33.50	do	Des Moines, Iowa	
10	38.57	Michigan	Ames, Iowa	
11	36.67	Illinois	do	
12	37.55	Unknown	Moscow, Idaho	
13	38.60	do	Bozeman, Mont	
14	38.59	do	do	
15	36.93	do	do	
16	37.11	England	Columbus, Ohio	
17	35.54	Unknown	do	
18	36.55	do	Dayton, Ohio	
19	37.26	do	Indianapolis, Ind	
20	25.75	Germany	San Francisco, Cal	Heavy precipitate.
21	37.43	Unknown	do	
22	37.45	do	do	
23	39.11	do	do	
24	38.70	do	do	
25	36.20	do	Pullman, Wash	Of jelly-like consistency.
26	36.25	Pennsylvania		From stock of Bureau of Chemistry.
27	37.55	Germany		
28	37.25	do		
29	36.55	do		

The results of this single investigation indicate that the amount of formaldehyde contained in the preparation sold in the United States averages approximately 37 per cent. Some of these samples, particularly those obtained from the far Western States, contained large quantities of insoluble polymerized formaldehyde, the correspondents from these States writing that it was very difficult to obtain samples not having such a precipitate. It is difficult to explain why this condition should obtain in the Pacific Coast States. In one or two of these samples, particularly in the one from Pullman, Wash., the volume of precipitate continued to increase until the contents of the bottle became a jelly-like mass. Formaldehyde in this condition is of little use as a disinfectant unless used in a steam autoclave, and as a fungicide it is valueless, for when the white precipitate has once formed it is very insoluble, and it is impossible to tell, without an analysis, what percentage of active substance is available in the solution.

Chlorid of Lime.

The value of bleaching powder depends upon its percentage of available chlorin, and a number of satisfactory methods have been suggested for its determination. Those sent out by the referee were Penot's, in which an arsenite is oxidized to an arsenate, and that of J. Pontius, which depends upon the oxidation of iodids to iodates by means of hypochlorous acid and the liberation of iodin from iodids by means of iodates. The directions as sent out follow:

PREPARATION OF CHLORINATED LIME SOLUTION.

Weigh 7.1 grams, triturate finely with a little water, add gradually more water; pour the liquid into a liter flask, triturate the residue again with water and rinse the contents of the mortar carefully into the flask. Fill to the mark, shake the milky fluid and examine it at once in that state, and every time before measuring off a fresh portion shake again.

Method 1. (*Penot's.*) [a]

PREPARATION OF REAGENTS.

Potassium-iodid-starch paper.—Stir 3 grams starch in 250 cc of cold water, boil with stirring, add a solution of one gram of potassium iodid and one gram of crystallized sodium carbonate and dilute to 500 cc. Moisten strips of fine white unsized paper with this fluid and dry. Keep in closed bottle.

Solution of arsenious oxid.—Dissolve 4.95 grams of C. P. arsenious oxid and about 20 grams of pure sodium carbonate in 600–700 cc of water, cool, and dilute to one liter.

Procedure.—Measure off with a pipette 50 cc of the solution of chlorinated lime, transfer to a beaker and from a 50 cc burette add slowly, and at last drop by drop, the solution of arsenious oxid, with constant stirring, until a drop of the mixture produces no longer a blue colored spot on the iodized paper. Each cubic centimeter used indicates a percentage of available chlorin.

Method 2. (*Pontius.*)[b]

Fifty cc of the solution prepared as above (7.1 grams to liter) are measured off into a beaker containing 3 grams of solid sodium bicarbonate, which reacts with calcium salts with formation of calcium carbonate, sodium chlorid, and hypochlorous acid. After stirring well, 1 or 2 cc of starch solution is added, and the liquid immediately titrated with potassium iodid solution (containing 3.7667 grams of potassium iodid per liter, one-sixth of a molecule of potassium iodid being required for one atom of chlorin) until the blue color produced is permanent. The number of cubic centimeters used gives the per cent of available chlorin.

As potassium iodid is never quite 100 per cent pure this solution should be carefully standardized.

TABLE VII.—*Available chlorin.*

Analyst.	Date of analysis.	Method 1.	Date of analysis.	Method 2.
		Per cent.		*Per cent.*
B. H. Smith, Bureau of Chemistry	1904. December 19	27.90 27.85 27.80	1904. December 19	28.11 28.06 28.06
J. H. Norton, Fayetteville, Ark	1905. January 18	27.35 27.65	1905. January 18	28.35 28.35 28.35
R. W. Thatcher, Pullman, Wash	January 20	27.30 27.32 27.56	January 20	27.65 27.60 27.86 27.84
J. R. Moechel, Kansas City, Mo	March 20	26.30 26.38 26.36 26.39	April 27	25.40 25.35 25.36 25.36
B. H. Smith, Bureau of Chemistry	October 18	19.50 19.52	October 16	19.55 19.66

COMMENTS OF ANALYST.

R. W. Thatcher: Method 2 gave slightly higher results than Method 1. The potassium iodid solution used in Method 2 was carefully standardized, using Volhard's method of titrating with standard silver nitrate.

DISCUSSION.

In comparing the results of the table it is necessary to bear in mind that the available chlorin in chlorid of lime continually decreases on standing, largely due to chemical changes within the product itself. Taking the dates of analysis into consideration and the fact that slight differences in temperature exert a marked influence upon the percentage of this constituent the results are very satisfactory.

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[a] Fresenius, 6th ed., *11:* 379.

[b] Chem. Zeit., *28:* 59

PHENOLIC DISINFECTANT.

This sample was examined by a method given in Allen's Commercial Organic Analysis,[a] but the results obtained were so divergent that they are not given.

RECOMMENDATIONS.

It is recommended—

(1) That Methods I and II (being Methods I and IV of last year's report) of the four modifications of the Avery-Beans method of determining total arsenic in Paris green be adopted as optional official methods.

(2) That in titration of arsenic N/20 instead of N/10 iodin be used.

(3) That the work on London purple be continued.

(4) That the thiosulphate method of determining copper, using N/20 instead of N/10 thiosulphate be adopted as an optional method.

(5) That the hydrogen peroxid method for determining sulphur in sulphur dips and similar compounds be further tested, an effort being made to have all analyses made simultaneously.

(6) That the hydrogen peroxid method for determining formaldehyde be tested in its modified form.

(7) That the methods of determining available chlorin in bleaching powder be further compared.

THE DETERIORATION OF BLEACHING POWDER.

By BERNARD H. SMITH.

The chemist who has occasion to use bleaching powder knows that the average sample taken from the laboratory shelf is apt to contain a low percentage of available chlorin. Recently when two cans from the stock of the Bureau of Chemistry were examined they ran but 9 and 13 per cent. While this inferiority is due largely to the low standard of the original article, it is partly caused by the chemical changes continually taking place within the product, which result in a constantly increasing amount of chlorid at the expense of the available chlorin.

Some years ago Mr. John Pattinson[b] conducted an investigation to determine the rapidity with which bleaching powder deteriorates, both in the large iron drums in which it is shipped and stored, and in small corked bottles. He concluded that the available chlorin of bleaching powder disappears in proportion to the length of time it is kept and to the temperatures to which it is subjected, yet within a comparatively small amount the whole of the chlorin it originally contained is still retained combined in some form with the calcium of the compound. This being true, when one finds a bleaching powder that runs lower than it should in available chlorin, by making a determination of the total chlorin present a very correct opinion may be formed as to whether or not the sample contained the standard percentage originally.

The writer believed it would be of interest to compare results obtained upon the same sample when kept in the ordinary commercial retainers and in sealed bottles, and also to compare samples of different brands kept under similar conditions. The work has been carried out upon four samples, two of which have been under examination for a year. For each analysis, a fresh bottle or can has been used and the temperature, though slightly higher during the summer months, has not been far from 70° F. throughout the period. The following table summarizes the results obtained:

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[a] Ed. 3, vol. 2, pt. 2, 262.

[b] J. Soc. Chem. Ind., 1888, 7: 188.

TABLE I.—*Decrease of available chlorin in bleaching powder.*

DESCRIPTION OF SAMPLE.

No. of sample.	Source of sample.	Container.
I.	Purchased at drug store; manufacturer unknown	Sealed bottles.
II.	Imported by New York firm, who furnished sample	Sealed bottles; cans.
III.	Furnished by Philadelphia firm; said to be manufactured by the Castner electrolytic process at Niagara Falls.	Cans.
IV.	Manufactured and furnished by a chemical company of Midland, Mich.	Sealed bottles.

RESULTS OF ANALYSIS.

Date.	Sample I.	Sample II.		Sample III.	Sample IV.
		Sealed bottles.	Cans.		
1904.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
October	30.40				
November	28.90	33.20	33.20		
December	28.20	32.20	32.15		
1905.					
January	27.85	31.20	31.15		
February	27.00	31.00	30.90	37.00	
March	26.40	30.50	30.40	34.05	
April	25.95	30.20	30.10	32.00	41.9
May	25.40	30.00	29.85	31.05	
June	23.85	29.20	29.00	29.45	41.10
July	22.90	28.10	28.00	28.30	39.10
August	Not determined.				
September	20.80	25.80	25.60	[a] 25.90	38.40
October	19.60	25.00	24.80	[a] 24.75	38.26

[a] Can corroded and porous.

Samples I and II seem very dry and more or less granular in appearance; the last two samples have the appearance of being more moist and pack and lump up readily. On a complete analysis, however, they do not appear to contain more water or vary essentially in any other ingredient.

TABLE II.—*Complete analyses of the samples described in Table I.*[a]

Constituents determined.	Sample I.	Sample II.	Sample III.	Sample IV.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Calcium	31.23	32.32	31.63	28.17
Magnesium	.32	.48	.54	.11
Iron and aluminum	.74	.18	.70	.59
Chlorin:				
As available	26.10	30.20	32.00	41.90
As chlorid	9.40	4.90	5.80	1.20
As chlorate	.80	.50	1.20	.10
Carbonic acid ion (CO_3)	.19	2.02	.60	.82
Silica (SiO_2)	.47	.32	.38	.25
Water	17.40	16.16	15.30	15.85
Oxygen required	13.35	12.92	11.85	11.01

[a] Analyses made in April, 1905.

Sample II was received in zinc cans which are yet well preserved; sample III was forwarded in iron (tin covered) cans, the last one of which was eaten through in October, 1905. The latter, however, is not regularly shipped in these cans, but was packed in this way by request. Regarding this sample, the firm furnishing it states that "The bleach of which we sent you a sample is as good a bleach as we have ever used for manufacturing. All electrolytic bleach, however, loses strength very rapidly on the opening of the container."

Evidently very little chlorin is lost from the commercial zinc can, judging from the two sets of results on sample II. Sample IV, while very high in chlorin content, has not deteriorated as rapidly as would be expected. The one thing that is made strikingly plain by this work is that the purchaser when buying chlorid of lime should insist upon getting a fresh article.

A STUDY OF THE LIME-SULPHUR-SALT-SODA WASH.

By J. K. Haywood.[a]

In a study recently made by the author[b] concerning the composition of the lime-sulphur-salt wash, prepared according to the following formula: Lime, 10 pounds; sulphur, $6\frac{2}{3}$ pounds: salt, 5 pounds; and water, 20 gallons, it was found that a 60-minute period of boiling is sufficient to get practically all sulphur in solution and that the composition of the wash at this time (after 60 minutes) is as follows, when the evaporated water is replaced by a like amount after the mixture cools.

Table I.—*Lime and sulphur in 100 cc of the lime-sulphur-salt wash.*

	Grams.
Sulphur in solution	3.75
Residual sulphur	.05
Total sulphur	3.80
Calcium oxid in solution	2.13
Residual calcium oxid	3.42
Total calcium oxid	5.55

A determination of the sulphur compounds in the liquid portion of this wash boiled for the same length of time gave the following results:

Table II.—*Sulphur compounds in 100 cc of the liquid portion of the lime-sulphur-salt wash.*[c]

	Grams.
Sulphur as thiosulphates	0.84
Sulphur as polysulphids and sulphids	2.91
Sulphur as sulphites and sulphates	.01
Total sulphur	3.76

A study of the decomposition products of this wash was then made by determining the products obtained on soaking up a weighed quantity of the wash with strips of filter paper, allowing them to dry and then standing them in the open air for varying lengths of time. In this experiment some of the samples were left dry for the entire period while some were sprinkled with water each day to represent dew. One would be inclined to believe *a priori* that this mixture of sulphur compounds on drying and weathering would break up in the following way: First, the penta-sulphid would be oxydized to thiosulphate and sulphur set free according to the formula $CaS_5+3O=CaS_2O_3+3S$. Second, the thiosulphate thus formed, together with the thiosulphate originally present in the solution, would then change to sulphite and free sulphur according to $CaS_2O_3=CaSO_3+S$. Third, the sulphite would then be oxydized slowly to sulphate.

One would expect to find in the wash then, after it had dried on the tree, free sulphur, thiosulphate, and small quantities of sulphite and sulphate. The longer the action of the air and dew continued the less thiosulphate one would expect to find and the more sulphur, sulphites, and sulphates. Finally, only free sulphur and sulphates would be present. That such reactions as the above take place and that they are hastened by wetting the mixture of sulphur compounds each day is shown by the figures in the following table:

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[a] Credit is due Mr. B. H. Smith for assisting in the analytical work.

[b] J. Amer. Chem. Soc., 1905, *27:* 244.

[c] The reactions that very likely take place between the lime and sulphur to form these compounds are given in the original article just mentioned.

Table III.—*Sulphur compounds formed on tree (filter paper) by decomposition of the wash.*

[Expressed in grams per 100 cc of wash used.]

NOT WATERED.

Time of standing.	Free sulphur.	Sulphur as thiosulphate.	Sulphur as sulphite.	Sulphur as sulphate.	Total sulphur.
Days.					
5	1.71	1.97	0.11	0.01	3.80
5	1.72	1.97	.10	.01	3.80
8	1.74	1.94	.13	.01	3.83
8	1.77	1.94	.12	.02	3.85

WATERED TO REPRESENT DEW.

Time of standing.	Free sulphur.	Sulphur as thiosulphate.	Sulphur as sulphite.	Sulphur as sulphate.	Total sulphur.
10	1.94	1.66	0.22	....	3.82+
10	1.93	1.69	.20	....	3.82+
28	2.11	1.42	.29	0.15	3.97
28	2.13	1.41	.27	.16	3.97

In the following investigation the author has made a study of the recently proposed lime-sulphur-salt and soda wash along the same lines as laid down above, to find whether it differs materially in composition from the old lime-sulphur-salt wash. This wash is prepared with sodium hydroxid so as to dissolve the sulphur without any boiling at all or with a miminum amount of boiling. The formula used in preparing this wash and the method of preparing it are as follows:

Ten pounds of lime, 6⅔ pounds of sulphur, 5 pounds of salt, and 3⅓ pounds of caustic soda (98 per cent) are used. The sulphur is made into a paste with 3 quarts of hot water, the lime is slaked with three gallons of hot water, and the sulphur paste is added to it. Then the caustic soda is added and stirred in and the mixture boils of itself for a considerable period. Salt is then added and the requisite amount of water added to make up to 20 gallons plus the space occupied by the solids (as determined by experiments). To test the effect of heating this mixture for a short time after it has ceased to boil of itself and has cooled down, the same procedure is followed as above except that the mixture as finally prepared is heated slowly for 20 minutes so as to just bring it to a boil in this length of time.

The results obtained on the whole mixture by these two methods of preparation are given in the following table:

Table IV.—*Lime and sulphur*[a] *in 100 cc of the lime-sulphur-salt-soda wash.*

Constituents.	First method.	Second method.	
	Grams.	*Grams.*	*Grams.*
Sulphur in solution	3.25	3.74	3.84
Residual sulphur	.30	.08	.02
Total sulphur	3.55	3.82	3.86
Calcium oxid in solution	.73	.75	.75
Residual calcium oxid	4.82	4.08	4.80
Total calcium oxid	5.55	5.55	5.55

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[a] A determination of the sodium hydroxid present was thought to be unnecessary, as this substance would of course all go into solution either as caustic soda or as sodium salts of the sulphur acids.

Since it is evident from Table IV that such a procedure as the first one outlined does not get all sulphur in solution while such a procedure as the second, i. e., bringing to a boil in 20 minutes, does get practically all sulphur in solution, a study of the different sulphur compounds in the liquid portion of the wash was only made in a wash prepared by the second method. The results are given in the following table:

TABLE V.—*Sulphur compounds in 100 cc of the liquid portion of the lime-sulphur-salt-soda wash.*

	Grams.
Sulphur as thiosulphates	0. 88
Sulphur as polysulphids and sulphids	3. 04
Sulphur as sulphates and sulphites	. 005
Total sulphur	3. 925

It is evident from Tables IV and V, first, that all sulphur does not go in solution in the lime-sulphur-salt-soda wash as usually prepared; second, that practically all sulphur does go into solution when this wash is heated for twenty minutes; third, that the composition of this wash when heated for twenty minutes so as to get all sulphur in solution is practically the same as the lime-sulphur-salt mixture in so far as the sulphur acids present are concerned; fourth, that the only difference between these two washes seems to be, first that the sulphur compounds in the lime-sulphur-salt-soda wash are present to a large extent as the sodium salts instead of the calcium salts, thus causing a smaller amount of lime to go into solution and a larger amount to remain as a residue, and, second, that the lime-sulphur-salt-soda wash is more caustic on account of the presence of the caustic soda.

A study was next made of the decomposition of this wash along the lines already laid down earlier in this paper. The results of this work follows:

TABLE VI.—*Sulphur compounds formed on tree (filter paper) by decomposition of the lime-sulphur-salt-soda wash.*

[Expressed in grams per 100 cc of the wash used.]

NOT WATERED.

Time of standing.	Free sulphur.	Sulphur as thiosulphate.	Sulphur as sulphite.	Sulphur as sulphate.	Total sulphur.
9 days	1. 57	2.27	0.02	0.00	3.86
28 days	1. 64	2.14	.06	.02	3.86

WATERED TO REPRESENT DEW.

Time of standing.	Free sulphur.	Sulphur as thiosulphate.	Sulphur as sulphite.	Sulphur as sulphate.	Total sulphur.
12 days	1. 64	2. 19	0. 04	0. 01	3. 88
27 days	1. 74	1. 88	. 10	. 02	3. 74

From the above table it is evident that the lime-sulphur-salt-soda wash decomposes in the same manner as the lime-sulphur-salt wash except that the rate of decomposition is evidently much slower. Since the above is true it would appear, on purely chemical grounds, that the wash with caustic soda added ought to give just as good results as the original lime-sulphur-salt wash if properly prepared. In fact, better results might be expected since the sodium hydroxid is more caustic than the lime and would therefore tend to loosen the scale better so that the other ingredient of the wash could act more thoroughly. However, two points must be taken into consideration. First, sodium sulphite, which is undoubtedly formed to some extent, is more soluble than calcium sulphite, so that in a damp climate it would be washed off more easily. (Since the sulphite is very likely of great importance in the wash, this point is worthy of consideration.) Second, the rate of decomposition of the lime-sulphur-salt-soda wash is slower than that of the lime-sulphur-salt wash, so that it is just possible that such decomposition might not be fast enough to be as efficacious as the old wash, assuming, of course, that the decomposition products have insecticidal properties. In expressing the above opinions the author does so purely on chemical grounds and of course recognizes that field experiments are necessary to establish the truth or falsity of his conjectures.

In the lime-sulphur-salt-soda wash the author is unable to see that anything is gained by the addition of salt.[a] Besides this it would appear that the caustic soda entirely takes the place of the lime in so far as the caustic action of the wash on the scale is concerned. Therefore, a wash composed only of sulphur, caustic soda, and water seems worthy of trial. Such a wash should of course have approximately the strength of the old lime-sulphur-salt wash and should, besides, require absolutely no heating to get the sulphur in solution. After a number of trials of different relative proportions of caustic soda, sulphur, and water, it was found that if the formula as given below is used a mixture will be formed having in solution approximately the same amount of sulphur and the same sulphur compounds as the original lime-sulphur-salt wash, with this exception, that these sulphur compounds exist entirely as the sodium salts instead of being to a large extent calcium salts.

Proposed formula.

Water	gallons	20
Powdered sulphur	pounds	7¾
Caustic soda (98 per cent)	do	4

Directions.—Make a paste or gruel of the sulphur with 2¼ gallons of boiling water; at once add all the caustic soda, which has been previously broken up into pieces the size of a hickory nut or walnut, and stir occasionally for half an hour; at the end of this time add 17¾ gallons of water, stir, and the wash is ready for use.

This wash on analysis for sulphur compounds shows the following composition:

TABLE VII.—*Sulphur compounds in 100 cc of the caustic soda, sulphur wash.*

	Grams.
Sulphur as thiosulphates	0.63
Sulphur as polysulphids and sulphids	2.85
Sulphur as sulphates and sulphites	.01
Total sulphur	3.49

It will be noted that this wash is somewhat weaker than the original lime-sulphur-salt wash, but not enough in the author's opinion to make any material difference. However, if others are of the opinion that it should be of exactly the same strength it can easily be made so by adding 15¾ gallons instead of 17¾ gallons of water, as given in the formula. Such a wash as the above is slightly more costly than the lime-sulphur-salt-soda wash as usually recommended, but the difference in cost is small, amounting only to the cost of two-thirds of a pound of caustic soda and 1⅓ pounds of sulphur per 20 gallons.

Mr. Davidson asked whether any experiments had been tried with the lime and sulphur without salt, to which Mr. Haywood replied that the salt did not change the composition of the wash and had been found by some experiment stations to be without value. The president inquired as to the utility of using heat in preparing the lime-sulphur-salt wash and Mr. Haywood replied that heat seemed to be necessary to get the proper amount of sulphur in solution, the heating to be continued for about one hour. In response to the question whether the sulphid of soda should be bought on the market or prepared by the farmer himself, Mr. Haywood said:

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[a] It has been suggested by Mr. F. K. Cameron, of the Bureau of Soils, that the lime in the wash reacts with the sodium chlorid to some extent according to the following reaction, $Ca(OH)_2+2\ NaCl \gtrless 2\ NaOH+CaCl_2$ thus resulting in the formation of calcium chlorid, which by its hygroscopic properties causes the wash to stick to the tree. While the author recognizes that this reaction would take place to same extent, it would hardly, it seems, be to a sufficient extent to cause the formation of enough calcium chlorid to be of any great value. Besides this, recent field experiments at a number of experiment stations have shown that the wash is just as efficacious without the salt as with it.

> I would suggest that the fruit grower make it himself for two reasons: First, it is not the sodium sulphid alone that is present, but a mixture of the sulphid or polysulphid of soda with the sodium thiosulphate and small amounts of other sulphur compounds, and we do not know just which of these compounds it is that produces the effect; second, it is much cheaper to prepare the wash from soda and sulphur, and as no boiling is necessary with this mixture the only objection made by the farmer is removed. As to the possibility of injuring the trees it is believed that the use of 4 pounds to 20 gallons of water will not cause the slightest injury, as it is applied to trees when dormant, and further much larger quantities are used when sodium hydroxid alone is applied, and no injury results. It is suggested that the experiment stations could profitably study the various compounds of which the soda-sulphur wash is composed, thus determining which are effective and eliminating the unnecessary constituents.

Mr. Smith, of the Michigan Station, stated that the determination of a satisfactory wash that could be made without boiling would be worth many thousands of dollars to the Michigan farmer.

THURSDAY—AFTERNOON SESSION.

The report on foods and feeding stuffs was called for and the associate stated that as far as he knew no work on the subject had been done. The report on food adulteration was then introduced by Mr. Bigelow.

REPORT ON FOOD ADULTERATION.

By W. D. Bigelow, *Referee.*

Up to the present time the work that has been done in the elaboration of methods for the examination of foods has been largely of an individual nature. The greater part of the work has been done by the associate referees to whom the subjects were assigned. It is believed, however, that now the ground has been very well covered and that the time has come when progress can best be made by collaborative work as has been done along other lines by the association.

We have always found that collaboration from men thoroughly experienced in any line of work is difficult to obtain, and for this reason further progress must be relatively slow. I hope, however, that those members of the association whose duties include the examination of foods with reference to their quality and purity will now find time to participate in collaborative work for the purpose of further proving the methods which have been provisionally adopted by the association, and perfecting the details of those methods.

During the past year progress has been made in several subjects. Important collaborative work has been conducted on the subject of fats and oils in the study of the titer test and the cold test. Under the subject of dairy products a new method has been suggested and carefully tested for the detection of added water in milk. All of the methods for the examination of distilled liquors have been carefully studied, and considerable collaborative work on that subject has been done leading to various suggestions for the improvement of those methods. The methods for the examination of maple sirup and maple sugar have been further studied and considerable advance made. The work on spices has been extended to include the examination of prepared mustard. The associate referee on colors, Mr. Berry, has completed an extensive preliminary report, chiefly in the nature of a compilation, which has been published as Circular No. 25 of the Bureau of Chemistry, under the title "Coloring matters for food stuffs and methods for their detection." The study of methods for the detection and quantative determination of preservatives has also been continued.

I would suggest, Mr. President, that these subjects be considered in order and that the several associate referees charged with the various sections of the work be asked to present their reports.

REPORT ON FRUIT PRODUCTS (DETERMINATION OF WATER IN DRIED FRUITS).

By E. Monroe Bailey, *Associate Referee.*

The work upon fruit products has been confined to an effort to evolve a practical method for the determination of water in dried fruits. The literature already gives some idea as to methods of analysis, and affords considerable analytical data. Bertram[a] dried the material directly at 100°. When sufficient moisture was removed, he ground the residue in a mortar and completed the drying at the temperature mentioned. Colby and Dyer[b] have worked with dried fruits, and their analyses include prunes (French), apricots, figs, grapes, apples, and raisins. Kickton[c] has analyzed dried apricots and has published his methods and results. His method for the determination of water is like that of Bertram. König's[d] compilation includes analyses of dried fruits and represents the work of numerous analysts, including those herein mentioned, except Kickton. An abstract from his compilation will be found in Table I.

Table I.—*Water content of various dried fruits* (*König*).

Variety.	Number of analyses.	Maximum.	Minimum.	Average.	Variety.	Number of analyses.	Maximum.	Minimum.	Average.
		Per ct.	*Per ct.*	*Per ct.*			*Per ct.*	*Per ct.*	*Per ct.*
Apples	4	36.20	23.48	31.28	Grapes	28	37.83	14.00	24.46
Pears	3	32.86	25.77	29.41	Currants	8	27.60	14.35	25.35
Plums	11	42.62	12.99	28.07	Figs	9	40.36	21.06	28.78
Apricots	2	32.44	32.40	32.42	Dates	2	20.33	16.68	18.51
Huckleberries	1	....	....	9.14	Bananas	1	....	....	29.17
Cherries	1	....	....	49.88					

Analysts appear to experience a common difficulty in obtaining constant weights of acidulated, sugar-containing residues, and hence accurate figures for water content, but inasmuch as for purposes of food control comparative results by a practical method are of greater value than absolute results by an involved method, it seems desirable to make the course of procedure simple, even though the results obtained may vary slightly from the truth. Accordingly two simple methods were tried upon four commercial dried fruits, viz, prunes, peaches, apricots, and apples. In the case of prunes the stones were removed. In all cases the material was reduced to a uniform mechanical condition by passing it twice through a universal meat chopper.

Method I.

Ten grams of the hashed material were weighed out into a flat-bottomed aluminum dish 8 cm in diameter, and dried at 100° C. in a steam oven, weighings being taken at intervals of eight hours. In all cases the material was allowed to cool in a desicator for at least an hour before weighing.

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[a] Landw. Versuchs.-Stat. 1876, *19:* 401.

[b] Cal. Exper. Stat. Rep., 1892–93 and 1893–94.

[c] Zts. Nahr. Genussm., 1904, *8:* 675–678.

[d] Chemie der menschlichen Nahrungs- und Genussmittel, 4th ed., *1:* 863–868.

METHOD II.

Drying with sand having given satisfactory results in the case of jams and jellies,[a] this method was tried with dried fruits. In a flat-bottomed aluminum dish provided with a glass rod, both having been weighed together, were placed ten grams of the hashed material. Warm water was then added and the mass worked to the consistency of jam. Forty grams of ignited sand were mixed intimately with the contents of the dish, and the whole allowed to evaporate upon a water bath with constant stirring to prevent the formation of lumps. The mass was afterwards further dried at 100°C. in a steam oven, weighings being taken at eight hour intervals as before. The results of duplicate determinations by each of these two methods appear in Table II.

TABLE II.—*Results of water determinations in dried fruits.*

Material.	Time of drying—hours.					Increments.			
	12.	20.	28.	36.	44.	12–20.	20–28.	28–36.	36–44.
Prunes, with sand:	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Sample No. 1	25.82	26.63	27.22	27.83	28.15	0.83	0.59	0.55	0.31
Sample No. 2	25.87	26.73	27.31	27.80	28.11				
Average	25.85	26.68	27.27	27.82	28.13				
Prunes, without sand:									
Sample No. 1	24.04	25.62	26.58	27.23	27.56	1.27	.79	.68	.40
Sample No. 2	23.95	24.92	26.13	26.84	27.31				
Average	24.00	25.27	26.36	27.04	27.44				
Peaches, with sand:									
Sample No. 1	24.81	25.88	26.68	27.11	27.85	.75	.88	.48	.67
Sample No. 2	25.31	25.74	26.70	27.22	27.83				
Average	25.06	25.81	26.69	27.17	27.84				
Peaches, without sand:									
Sample No. 1	23.38	23.78	25.41	26.35	27.22	1.18	1.52	.89	.83
Sample No. 2	23.07	25.19	26.45	27.28	28.08				
Average	23.23	24.41	25.93	26.82	27.65				
Apricots, with sand:									
Sample No. 1	32.99	34.29	35.74	36.34	36.85	1.29	1.41	.59	.49
Sample No. 2	32.96	34.24	35.61	36.19	36.67				
Average	32.98	34.27	35.68	36.27	36.76				
Apricots, without sand:									
Sample No. 1	33.12	34.32	35.09	35.98	36.72	1.21	.75	.88	.92
Sample No. 2	33.07	34.30	35.03	35.90	37.00				
Average	33.10	34.31	35.06	35.94	36.86				
Apples, with sand:									
Sample No. 1	24.38	25.82	27.17	27.91	28.58	1.42	1.33	.73	.67
Sample No. 2	24.41	25.82	27.12	27.85	28.52				
Average	24.40	25.82	27.15	27.88	28.55				
Apples, without sand:									
Sample No. 1	24.43	25.57	26.14	27.10	27.47	1.12	.59	.95	.35
Sample No. 2	24.66	25.76	26.38	27.31	27.68				
Average	24.55	25.67	26.26	27.21	27.58				

CONCLUSIONS.

From the results recorded in Table II it appears that: (1) Duplicates by the same method agree with reasonable accuracy, showing that errors due to sampling are inconsiderable. (2) Duplicates by the two different methods agree approximately; drying with sand gives slightly higher and presumably more accurate results, but the increased accuracy does not seem to warrant the expenditure of the extra labor and time involved in the process. It is quite possible that increasing the amount of sand would produce more striking results and perhaps throw the balance of favor more decidedly toward this method. (3) Although it appears that the material can lose weight indefinitely, it seems reasonable to discontinue the heating when the increment in the amount of water obtained for an eight-hour period becomes approximately three-fourths of 1 per cent. The following course of procedure will therefore serve all practical purposes:

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[a] Winton, A. L., et al., Conn. Exper. Stat. Food Rep., 1898, pp. 109–110.

Free the material from core or stone if necessary and reduce it to a uniform mass by passing it twice through a meat chopper. Weigh out 10 grams of the hashed material into a flat-bottomed aluminum dish, 8 cm in diameter and dry for thirty hours at 100° C. Cool in a desiccator for at least an hour and weigh. The loss in weight may be reckoned as the water content.

In this connection Mr. Frear called attention to the work done at the Pennsylvania station in drying materials in the nutrition work and the danger of decomposition by the ordinary methods of drying, and further described some work done in drying in vacuo according to the method of Benedict, asking that this method be further studied by the referee in 1906. Mr. Wiley called attention to Maquenne's method, lately published in the Comptes Rendus, and suggested that this method also be made the subject of study, stating that for many years the vacuum oven had been in common use in the Bureau of Chemistry for drying. Mr. Bigelow called attention to the difficulties of the problem of drying in the case of fruits, as illustrated in the work of the Bureau of Chemistry in the studies on the ripening of fruits, in which the temperature of the drying must not rise above 70° because of the danger of decomposition of the levulose.

As a result of this discussion the following motion, as made by Mr. Frear and amended by Mr. Wiley, was passed:

Resolved, That the referee on food adulteration be requested to provide next year for a systematic test of the method of Benedict and Manning [a] and of Maquenne's [b] method for determining hygroscopic moisture.

REPORT ON SACCHARINE PRODUCTS (MAPLE SUGAR AND SIRUP).

By Julius Hortvet, *Associate Referee.*

Two samples of maple sugar and two of sirup were sent out for cooperative work this year, to be examined according to the methods described by the referee in Circular No. 23 of the Bureau of Chemistry. Sample No. 1 was an Ohio sirup, No. 2 a Vermont sirup, while Nos. 3 and 4 were Vermont sugars from Bennington and Woodstock, respectively. The results reported by the analysts cooperating are given in the table following.

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[a] Amer. J. Phys., 1905, *13:* 309.

[b] Compt. rend., 1902. *135:* 208; 1905, *141:* 80.

TABLE I.—*Results of cooperative work on maple sugars and sirups.*

Analyst.	Sample.	1. Lead subacetate precipitate.	2. Ash.										3. Total ash				4. Malic acid value.
			a.	b.	c.	d.	e.	f.	g.	h.	i.	j.					
			Total.	Soluble.	Insoluble.	Alkalinity soluble ash.	Alkalinity insoluble ash.	Ratio insoluble to soluble ash.	Alkalinity 1 gram soluble ash.	Alkalinity 1 gram insoluble ash.	Ratio 1 gram insoluble alkalinity to 1 gram soluble alkalinity.	Ash soluble (on basis of total ash).	Manganese oxid (Mn_3O_4).	Calcium (CaO).	Sulphates (SO_3).	Potash (K_2O).	
		cc	*P.c.*	*P.c.*	*P.c.*	*cc* 10/N *HCl*	*cc* 10 N *HCl*		*cc* 10 N *HCl*	*cc* 10 N *HCl*		*P.c.*	*P.c.*	*P.c.*	*P.c*	*P.c.*	*P.c.*
C. H. Jones, Vermont	1[a]	1.00	0.54	0.35	0.19	0.44	0.45	1.84	126.0	237.0	0.53	65.0	0.64	23.98	1.06	38.02	0.41
	2[a]	2.40	.77	.47	.30	.63	.59	1.57	134.0	197.0	.68	61.0	.85	19.81	.68	35.90	.46
	3	....	.95	.59	.36	.77	.86	1.64	131.0	239.0	.55	62.0	....	.....	....	.....	.81
	4	....	.79	.52	.27	.70	.65	1.93	135.0	241.0	.56	66.0	....	.....	....	.....	.73
F. M. Hollister, Vermont	1	.85	.53	.35	.18	.52	.40	1.94	149.0	222.0	.67	66.0	....	.....	....	.....	....
	2	2.50	.75	.48	.27	.65	.60	1.78	135.0	222.0	.61	64.0	....	.....	....	.....	....
	3	3.50	.92	.55	.37	.77	.94	1.49	140.0	254.0	.55	60.0	....	.....	....	.....	....
	4	2.90	.80	.53	.27	.79	.74	1.96	149.0	274.0	.54	66.0	....	.....	....	.....	....
C. W. Nelson, Bureau of Chemistry	1	.40	.49	.308	.182	.36	.57	1.69	116.8	313.1	.373	62.8	.24	13.44	.20	.....	.93
	2	1.23	.683	.407	.276	.50	.62	1.47	122.8	224.6	.502	59.5	.52	13.16	.13	.....	1.26
	3	1.48	.944	.554	.39	.64	.79	1.42	115.5	202.5	.571	58.0	.26	13.38	.39	.....	1.21
	4	.89	.81	.491	.319	.60	.68	1.53	122.2	213.1	.573	60.6	.40	10.97	.16	.....	1.23
A. G. Woodman, Massachusetts	1	.59	.50	.31	.19	.35	.43	1.63	129.0	226.3	.499	62.0	....	.....	....	.....	.30
	2	1.31	.73	.45	.28	.51	.64	1.60	113.3	228.6	.496	61.6	....	.....	....	.....	.31
	3	2.67	.95	.61	.34	.65	.87	1.79	106.5	255.9	.416	64.2	....	.....	....	.....	.61
	4	1.97	.80	.52	.28	.61	.59	1.85	117.3	210.7	.557	65.0	....	.....	....	.....	.71
R. Hoagland, Minnesota	1	.71	.54	.37	.17	.36	.47	2.17	97.3	276.4	.352	68.5	....	.....	....	.....	.88
	2	1.24	.71	.45	.26	.50	.68	1.73	111.1	261.5	.424	63.3	....	.....	....	.....	1.00
	3	1.53	.88	.50	.38	.62	.84	1.31	124.0	221.0	.561	56.8	.28	19.07	1.98	31.42	1.01
	4	1.34	.77	.53	.24	.41	.61	2.20	77.3	254.1	.304	68.8	1.45	18.36	2.12	30.92	1.04
J. Hortvet, Minnesota	1	....	.....	.....	.....	.....	.....	....	.....	.....	......	....	....	.....	....	.....	....
	2	....	.....	.....	.....	.....	.....	....	.....	.....	......	....	....	.....	....	.....	....
	3	1.41	.95	.62	.33	.62	.93	1.88	100.0	281.8	.354	65.2	.81	21.99	1.31	33.25	1.01
	4	1.21	.74	.49	.25	.59	.77	1.96	120.4	308.0	.390	66.2	1.12	21.95	1.37	30.00	.99
H. C. Lythgoe, Massachusetts	1	2.15	.43	.28	.15	.38	.40	1.93	136.0	267.0	.50	65.1	....	.....	....	.....	....
	2	2.05	.57	.31	.26	.46	.56	1.19	148.0	226.0	.65	54.4	....	.....	....	.....	....
	3	3.70	.83	.49	.34	.56	.90	1.45	114.0	265.0	.43	59.0	....	.....	....	.....	....
	4	2.65	.74	.41	.34	.43	.67	1.21	95.0	197.0	.48	54.7	....	.....	....	.....	....

[a] Boiled and filtered sirups.

COMMENTS BY REFEREE.

There are wide discrepancies among the results under "lead subacetate precipitate," especially among the results obtained on the Ohio sirup. Two trials in this laboratory gave closely agreeing results, the lower being the one recorded, viz, 0.71 cc. Are the differences due to the character of the reagents used by the various analysts or are they due to different mechanical conditions? The referee has never regarded the method otherwise than as quick and approximate, and experience has shown that the results are fairly concordant on all samples which have been tested in this laboratory. The writer has never found a pure maple sirup giving a lower result than 0.94 cc. This Ohio sample appears to be all right by the other results obtained, especially in the ash analyses. It was noticed when first experimenting with the lead precipitate that the results were low when smaller amounts of the reagents were used or when the alumina cream was omitted. Goulard's lead subacetate is used and the alumina cream prepared according to the method given in Bulletin 46, Bureau of Chemistry, page 39. Results should agree quite closely if the tests are made under the same conditions.

Also, there are some peculiar variations among the results for malic acid. They seem too low in some instances, notably among the sirups. It may be that the results obtained in this laboratory are too high. We did the work very carefully, but there is possibly a source of error incidental to the dissolving and boiling of the ashed precipitate with the prescribed volume of standard hydrochloric acid. As stated by Jones, the effect of dilution of the sample previous to adding the alcohol is a factor to be considered. Better agreement in our results can be obtained when we adhere more strictly to the various steps of the method.

To illustrate the significance of the results obtained on the official samples, the following tabulation of analyses made on four brown sugars is given:

TABLE II.—*Analyses of four brown sugars.*

Ash.	Light.	Medium.	Medium.	Dark.
a. Total (per cent)	0.51	0.75	0.75	1.14
b. Soluble (per cent)	.44	.68	.61	.86
c. Insoluble (per cent)	.07	.07	.14	.28
d. Alkalinity soluble ash (cc N/10 HCl)	.30	.37	.27	.37
e. Alkalinity insoluble ash (cc N/10 HCl)	.16	.22	.39	.72
f. Ratio insoluble to soluble ash	7.28	11.20	4.35	3.07
g. Alkalinity 1 gram soluble ash (cc N/10 HCl)	67.0	53.9	44.2	43.0
h. Alkalinity 1 gram insoluble ash	246.0	351.0	278.0	257.0
i. Ratio 1 gram insoluble alkali to 1 gram soluble alkali	.27	.15	.16	.17
Ash soluble (per cent)	86.2	90.6	81.3	75.4
SO_3 (per cent)	5.16	4.56	4.06	2.38
Lead subacetate precipitate (cc)	1.90	2.59	2.15	2.40
Malic acid value	....	.19	.19	....

COMMENTS BY C. H. JONES.

The following ash determinations were made on official samples treated as indicated:

A. Ohio sirup No. 1, as received, 5 grams used.

B. Ohio sirup No. 1, boiled and filtered.[a]

C. Vermont sirup 2, boiled and filtered.[a]

D. Bennington sugar 3, boiled and filtered.[a]

E. Woodstock sugar 4, boiled and filtered.[a]

TABLE III.—*Results obtained after boiling and filtering sample.*

Ash.	*A.*	*B.*	*C.*	*D.*	*E.*
a. Total (per cent)	0.54	0.54	0.61	0.67	0.55
b. Soluble (per cent)	.36	.36	.37	.48	.40
c. Insoluble (per cent)	.18	.18	.24	.19	.15
d. Alkalinity soluble ash (cc N/10 HCl)	.48	.50	.66	.66	.54
e. Alkalinity insoluble ash (cc N/10 HCl)	.42	.46	.60	.50	.40
f. Ratio insoluble to soluble ash	2.00	2.00	1.54	2.53	2.67
g. Alkalinity 1 gram soluble ash (cc N/10 HCl)	133.00	139.00	178.00	138.00	135.00
h. Alkalinity 1 gram insoluble ash (cc N/10 HCl)	233.00	256.00	250.00	263.00	267.00
i. Ratio 1 gram insoluble alkali to 1 gram soluble alkali	.57	.54	.71	.53	.51
Per cent ash soluble	67.00	67.00	61.00	72.00	73.00
Lead subacetate precipitate [b]	....	1.00	2.40	1.80	1.50

[b] Vermont Agr. Exp. Stat. Report, No. 17, p. 454.

The use of 5 grams of sirup or sugar for ash determinations saves a large amount of time, and with pure goods the addition of small amounts of water to get rid of carbon is unnecessary and the characteristic network structure is not destroyed. A further fusion either with or without the use of water, while it may not change the result, destroys the identity of the ash.

The method of boiling and filtering, as I conduct it, is of great help with commercial samples. On the official samples as received the total ash varies from 0.54 to 0.95 per cent, while after the above treatment the range is from 0.54 to 0.67 per cent.

An insoluble ash of less than 0.15 per cent even on a boiled and filtered sample indicates admixture with cane or brown sugar, even though total ash be up to or above the minimum of 0.50 per cent.

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[a] Vermont Agr. Exp. Stat. Report, No. 17, p. 455.

The dilution of the sample previous to adding the alcohol appears to have a marked effect on the malic acid values. This is seen from the following tests made on the sirup samples No. 1 (Ohio) and No. 2 (Vermont):

TABLE IV.—*Effect of dilution of sample on the malic acid values*

Amount of sample.	Water added.	Malic acid values.	
		No. 1 (Ohio).	No. 2 (Vermont).
Grams.	*cc.*		
6.7	5	0.54	0.68
6.7	10	.46	.58
6.7	15	.41	.46
6.7	25	.43	.40

Mr. C. H. Jones discussed the work done at the Vermont Station on maple products, emphasizing the fact that the concordant results obtained by himself and Mr. Hortvet working independently were very satisfactory, and stating that it is now possible to detect adulteration with cane or brown sugar with great certainty. The examination of 150 samples of sugar and sirup for the purpose of establishing a standard for ash had given results leading Mr. Jones to agree with Mr. Hortvet that it was wise to leave that question open, relying upon a combination of results to establish the purity of the sample. A special method of boiling and filtering (used by Mr. Jones) was explained and reasons for its use given. It consists in getting about 40 grams of the sample into the form of a sirup boiling at 219° F., filtering hot, through double S and S 597 filters, without suction, and determining ash, malic acid value, and lead precipitate in the filtrate. Concluding, the speaker said that the main points of disagreement between the results of Mr. Hortvet and others were differences in the malic acid value, due, it is believed, to slight variations in handling the method, and suggested that the association consider this method the coming year.

REPORT ON DISTILLED LIQUORS.

By C. A. CRAMPTON, *Associate Referee.*

Under date of April 20, 1905, the associate referee sent the following circular letter to all analysts likely to cooperate in the work:

DEAR SIR: I would respectfully invite your collaboration in the study of methods for the analysis of distilled liquors for the Association of Official Agricultural Chemists.

I expect to send out four samples of liquors to each chemist undertaking the work, three of which will be of a similar character to those used last year, and one a sample to which methyl alcohol has been added.

Please inform me at your earliest convenience if you will take part in the work and desire a set of samples sent you. Further instructions will be forwarded with the samples.

Respectfully,

C. A. CRAMPTON,
Associate Referee on Distilled Liquors.

Favorable replies were received from sixteen analysts, and a corresponding number of samples were sent out accompanied by the following letter of instruction:

May 16, 1905.

Dear Sir: I have sent to your address to-day by express, through the Agricultural Department, a box containing four quart samples of distilled liquors (whisky) and a package of fuller's earth. The character of these samples is set forth in my letter dated April 20, and they are sent in accordance with your letter dated April —, expressing your willingness to cooperate.

You will please determine the percentage of alcohol, total solids, and fusel oil in each sample, and make such tests as will enable you to distinguish between the genuine and factitious liquors and to detect the presence of methyl alcohol in one of the samples. The general character of the work desired will be best indicated by a careful study of the report on this subject in last year's proceedings of the association, which will soon be published; also the recommendations in Circular No. 20, Bureau of Chemistry, Department of Agriculture.

The determination of alcohol should be made carefully, weighing the portion taken for distillation and the distillate, if possible. The determination of fusel oil should be made by the Roese method, as prescribed by the association. Determinations of acidity and of ethereal salts are also desirable. The various methods and tests for the presence of artificial coloring matter, as set forth in the above-mentioned report, should be carefully applied, and the results fully described.

An additional procedure is inclosed herewith, which proposes the use of amyl alcohol as a selective solvent for the natural coloring matter of spirits aged in wood. Procedures are also inclosed for Riche and Bardy's and Trillat's tests for the detection of methyl alcohol, both of which have been found more satisfactory than the Scudder and Mulliken test given in the provisional methods of the association under the head of flavoring extracts.

Please acknowledge the receipt of samples.

Your report, with results and suggestions, should be sent in not later than September 15.

Respectfully,

C. A. Crampton,
Associate Referee on Distilled Liquors.

Reports have been received upon nine sets of samples, and the results are included in the tabulation which follows. As indicated in the circular letter four samples were sent to each analyst, numbered simply 1, 2, 3, and 4:

No. 1. Genuine whisky, four years old, aged in wood.

No. 2. Factitious sample, made by mixing several trade whiskies.

No. 3. Same as No. 2, but with 10 per cent of pure methyl alcohol added.

No. 4. Artificial whisky made up in this laboratory entirely from neutral spirits by addition of caramel and flavoring extracts and with 0.25 per cent of pure amyl alcohol added.

The following table gives the results obtained by different analysts, including also the results of various tests applied to the samples, and the conclusions reached concerning the character of same:

TABLE I.—*Results of analyses of official samples of whiskies.*

[Calculated to a percentage basis.]

Analyst.	Specific gravity.	Solids.		Reducing bodies.	Ash.	Conclusions as to character of the samples analyzed.
		Total (extract).	H_2O soluble.			
Bureau of Chemistry:		*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	
Sample 1	0.93419	0.158		0.023	0.006	Straight uncolored whisky.
2	.93575	.144		.048	.002	Contains some whisky, but diluted with proof spirits, and colored by caramel.
3	.93835	.213		.029	.005	Also contains whisky, but diluted with proof spirits, methyl alcohol, and colored by caramel.
4	.93535	.113		.028	.0004	Purely artificial.
Joseph A. Deghuée:						
Sample 1	.9342	.149			.008	Straight whisky.
2	.9358	.224			.011	Contains added coloring matter.
3	.9385	.139			.004	Contains added coloring matter and methyl alcohol.
4	.9356	.117			.005	Colored alcohol and not a whisky at all.
A. Lasché:						
Sample 1		.150	70.50			
2		.199	82.34			
3		.142	75.91			
4		.108	93.26			
Leroy M. Law:						
Sample 1	.93434	.153		.044		Straight whisky.
2	.93578	.204		.084		Commercial.
3	.93812	.140		.052		Commercial with methyl alcohol added.
4	.93546	.108		.048		Factitious.
Clarence T. Marsh:						
Sample 1		.156				Straight whisky.
2		.212				Factitious; a mixture of spirits of different ages colored up.
3		.145				Factitious; straight whisky and methyl alcohol colored up.
4		.113				Factitious colored spirits not aged in wood.
McCandless, Williams, Burton:						
Sample 1		.136				Genuine whisky.
2		.196				Not all genuine; probably blended with factitious whisky.
3		.136				Not genuine; contains more factitious than No. 2, also contains wood alcohol.
4		.104				Wholly factitious.
Harris E. Sawyer:						
Sample 1	.93419	.145	.123			Straight whisky of good quality.
2	.93562	.167	.155			Colored somewhat; probably a blend of good quality.
3	.93861	.125	.107			Colored a little and "split" with methyl alcohol.
4	.93539	.104	.104			Entirely factitious.
R. E. Stallings:						
Sample 1	.93442	.164				Genuine.
2	.93550	.212				Obtained in market.
3	.93794	.142				Added methyl alcohol.
4	.93526	.107				Not a whisky.
L. H. Van Warmer:						
Sample 1	.93428	.162				Probably a pure whisky.
2	.93610	.215				About half-and-half.
3	.93834	.150				About one-quarter pure whisky.
4	.93549	.115				Entirely spurious.
Albert E. Leach:						
Sample 1[a]						
2	.9364	.2098			.005	Mixed whisky.
3	.9394	.1402			.004	Whisky with methyl alcohol.
4	.9361	.1084			.003	Factitious.

[a] This sample not received.

Table I.—*Results of analyses of official samples of whiskies*—Continued.

Analyst.	Color.				Conclusions as to character of the samples analyzed.
	Degree, of brewer's scale (¼″ cell).	Extracted by ether.	Extracted by chloroform.	Extracted by fuller's earth.	
		Per cent.	*Per cent.*	*Per cent.*	
Bureau of Chemistry:					
Sample 1	4.0		56.0		Straight uncolored whisky.
2	5.5		36.0		Contains some whisky, but diluted with proof spirits and colored by caramel.
3	5.5		30.0		Also contains whisky, but diluted with proof spirits, methyl alcohol, and colored by caramel.
4	4.0		.0		Purely artificial.
Joseph A. Deghuée:					
Sample 1				66.00	Straight whisky.
2				80.00	Contains added coloring matter.
3				80.00	Contains added coloring matter and methyl alcohol.
4				100.00	Colored alcohol and not a whisky at all.
A. Lasché:					
Sample 1		31.70	Nearly all.	64.20	
2		22.25	About ½.	71.90	
3		23.10	About ½.	67.60	
4		8.36	None.	84.70	
Leroy M. Law:					
Sample 1	5.0	36.30		62.50	Straight whisky.
2	6.5	28.50		73.00	Commercial.
3	4.5	22.20		77.00	Commercial with methyl alcohol added.
4	5.5	11.10		100.00	Factitious.
Clarence T. Marsh:					
Sample 1					Straight whisky.
2					Factitious; a mixture of spirits of different ages colored up.
3					Factitious; straight whisky and methyl alcohol colored up.
4					Factitious colored spirits not aged in wood.
McCandless, Williams, Burton:					
Sample 1				52.00	Genuine whisky.
2				74.00	Not all genuine; probably blended with factitious whisky.
3				74.00	Not genuine; contains more factitious than No. 2, also contains wood alcohol.
4				92.00	Wholly factitious.
Harris E. Sawyer:					
Sample 1		38.00		61.00	Straight whisky of good quality.
2		28.00		69.00	Colored somewhat; probably a blend of good quality.
3		28.00		71.00	Colored a little and "split" with methyl alcohol.
4		.00		92.00	Entirely factitious.
R. E. Stallings:					
Sample 1		35.00		60.00	Genuine.
2		17.00		64.00	Obtained in market.
3		12.50		67.00	Added methyl alcohol.
4		1.00		86.00	Not a whisky.
L. H. Van Wormer:					
Sample 1				58.31	Probably a pure whisky.
2				75.00	About half-and-half.
3				70.00	About one-quarter pure whisky.
4				100.00	Entirely spurious.
Albert E. Leach:					
Sample 1[a]					
2				Small.	Mixed whisky.
3				Small.	Whisky with methyl alcohol.
4				Large.	Factitious.

[a] This sample not received.

TABLE I.—*Results of analyses of official samples of whiskies*—Continued.

Analyst.	Alcohol.				Conclusions as to character of the samples analyzed.
	By volume.	By weight.	Degrees proof (real).	Proof from gravity.	
Bureau of Chemistry:	*Per cent.*	*Per cent.*			
Sample 1	50.12	42.58	100.24	100.20	Straight uncolored whisky.
2	49.33	41.83	98.66	98.62	Contains some whisky, but diluted with proof spirits, and colored by caramel.
3	48.16	40.75	96.32	95.88	Also contains whisky, but diluted with proof spirits, methyl alcohol, and colored by caramel.
4	49.06	41.58	98.12	99.04	Purely artificial.
Joseph A. Deghuée:					
Sample 1	50.31	42.76	100.62	100.18	Straight whisky.
2	49.50	42.00	99.00	98.58	Contains added coloring matter.
3	48.32	40.90	96.64	95.72	Contains added coloring matter and methyl alcohol.
4	49.61	42.10	99.22	98.80	Colored alcohol and not a whisky at all.
A. Lasché:					
Sample 1	50.92	43.46	101.84	100.25	
2	49.93	42.50	99.86	99.00	
3	48.45	41.10	96.90	96.50	
4	49.95	42.52	99.90	99.50	
Leroy M. Law:					
Sample 1	50.05	42.52	100.10	100.02	Straight whisky.
2	49.36	41.86	98.72	98.60	Commercial.
3	48.51	41.07	97.02	96.16	Commercial with methyl alcohol added.
4	49.47	41.96	98.94	98.94	Factitious.
Clarence T. Marsh:					
Sample 1	50.55	42.97	101.10	101.00	Straight whisky.
2	48.71	41.25	97.42	98.00	Factitious; a mixture of spirits of different ages colored up.
3	47.92	40.53	95.84	95.00	Factitious; straight whisky and methyl alcohol colored up.
4	47.60	41.22	95.20	97.00	Factitious colored spirits not aged in wood.
McCandless, Williams, Burton:					
Sample 1	53.25	45.56	100.50	....	Genuine whisky.
2	50.10	42.55	100.20	....	Not all genuine; probably blended with factitious whisky.
3	50.14	42.59	100.28	....	Not genuine; contains more factitious than No. 2, also contains wood alcohol.
4	51.19	43.59	102.38	....	Wholly factitious.
Harris E. Sawyer:					
Sample 1	50.19	42.65	100.38	100.12	Straight whisky of good quality.
2	49.50	42.00	99.00	98.65	Colored somewhat; probably a blend of good quality.
3	47.86	40.47	95.72	95.46	Colored a little and "split" with methyl alcohol.
4	49.52	42.02	99.04	98.89	Entirely factitious.
R. E. Stallings:					
Sample 1	50.38	42.82	100.76	99.96	Genuine.
2	50.30	42.74	100.60	98.90	Obtained in market.
3	51.00	43.41	102.00	96.32	Added methyl alcohol.
4	52.30	44.64	104.60	99.16	Not a whisky.
L. H. Van Wormer:					
Sample 1	50.05	42.52	100.10	100.10	Probably a pure whisky.
2	49.33	41.83	98.66	98.28	About half-and-half.
3	49.21	41.72	98.42	95.90	About one-quarter pure whisky.
4	49.72	42.20	99.44	98.90	Entirely spurious.
Albert E. Leach:					
Sample 1[a]	....	....	....	....	
2	49.29	41.80	98.58	97.92	Mixed whisky.
3	47.67	40.30	95.34	94.74	Whisky with methyl alcohol.
4	49.34	41.85	98.68	98.28	Factitious.

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[a] This sample not received.

TABLE I.—*Results of analyses of official samples of whiskies*—Continued.

Analyst.	Methyl alcohol.	Fusel oil.	Aldehyde.	Furfurol.	Ethereal salts.	Conclusions as to character of the samples analyzed.
Bureau of Chemistry:	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	
Sample 1	None.	[a]0.171	0.015	0.0032	0.048	Straight uncolored whisky.
2	None.	[a].120	.013	.0020	.033	Contains some whisky, but diluted with proof spirits, and colored by caramel.
3	[b]9.73	[a].057	.011	.0017	.025	Also contains whisky, but diluted with proof spirits, methyl alcohol, and colored by caramel.
4	None.	[a].208	.008	.0	.001	Purely artificial.
Joseph A. Deghuée:						
Sample 1	None.	.400	.0175	.0150	....	Straight whisky.
2	None.	.289	.0125	.0075	....	Contains added coloring matter.
3	Present.	(?)	.0100	.0007	....	Contains added coloring matter and methyl alcohol.
4	None.	.230	.0050	None.	....	Colored alcohol and not a whisky at all.
A. Lasché:						
Sample 1	None.	.136	.005	.0025	....	
2	None.	.177	.005	.0025	....	
3	Present.	.107	.007	.0025	....	
4	None.	.333	.001	None.	....	
Leroy M. Law:						
Sample 1	None.	.307	....	....	....	Straight whisky.
2	None.	.245	....	....	....	Commercial.
3	[b]10.92	(?)	....	....	....	Commercial with methyl alcohol added.
4	None.	.492	....	....	....	Factitious.
Clarence T. Marsh:						
Sample 1	None.	.332	....	.002	....	Straight whisky.
2	None.	.221	....	.001	....	Factitious; a mixture of spirits of different ages colored up.
3	20.00	(?)	....	.0008	....	Factitious; straight whisky and methyl alcohol colored up.
4	None.	Trace.	....	.0	....	Factitious colored spirits not aged in wood.
McCandless, Williams, Burton:						
Sample 1	None.	[a].1056	....	....	....	Genuine whisky.
2	None.	[a].0748	....	....	....	Not all genuine; probably blended with factitious whisky.
3	Present.	[a].0440	....	....	....	Not genuine; contains more factitious than No. 2, also contains wood alcohol.
4	None.	[a].1450	....	....	....	Wholly factitious.
Harris E. Sawyer:						
Sample 1	None.	.166	.009	.0015	[c]5.6	Straight whisky of good quality.
2	None.	(?)	.009	.0012	[c]4.3	Colored somewhat; probably a blend of good quality.
3	8.57	(?)	.007	.0010	[c]3.0	Colored a little and "split" with methyl alcohol.
4	None.	.219	.002	.0	[c].3	Entirely factitious.
R. E. Stallings:						
Sample 1	None.	.282	....	....	....	Genuine.
2	Small amt.	.298	....	....	....	Obtained in market.
3	Large amt.	(?)	....	....	....	Added methyl alcohol.
4	Trace.	.519	....	....	....	Not a whisky.
L. H. Van Wormer:						
Sample 1	None.	....	....	....	....	Probably a pure whisky.
2	None.	....	....	....	....	About half-and-half.
3	Yes.	....	....	....	....	About one-quarter pure whisky.
4	None.	....	....	....	....	Entirely spurious.
Albert E. Leach:						
Sample 1[d]	....	....	....	....	....	
2	None.	.2724	....	....	....	Mixed whisky.
3	10.01	(?)	....	....	....	Whisky with methyl alcohol.
4	None.	.1634	....	....	....	Factitious.

[a] These determinations not made by the association method.
[b] By volume.
[c] Cubic centimeters N/10 per 100 cc.
[d] This sample not received.

TABLE I.—*Results of analyses of official samples of whiskies*—Continued.

Analyst.	Tests, etc.						Conclusions as to character of the samples analyzed.
	Tannins.	Caramel (paraldehyde).	Caramel (amyl alcohol).	Character of color.	Taste.	Odor.	
Bureau of Chemistry:							
Sample 1	Yes		No.				Straight uncolored whisky.
2	Yes		Yes				Contains some whisky, but diluted with proof spirits, and colored by caramel.
3	Slight		Yes				Also contains whisky, but diluted with proof spirits, methyl alcohol, and colored by caramel.
4	None		Yes				Purely artificial.
Joseph A. Deghuée:							
Sample 1		None					Straight whisky.
2		None					Contains added coloring matter.
3		None					Contains added coloring matter and methyl alcohol.
4		Present					Colored alcohol and not a whisky at all.
A. Lasché:							
Sample 1		None	None				
2		Yes	Yes				
3		None	Yes				
4		Yes	Yes				
Leroy M. Law:							
Sample 1	Strong	No.	No.				Straight whisky.
2	Moderate	Yes	Yes				Commercial.
3	Moderate	Yes	Yes				Commercial with methyl alcohol added.
4	None	Yes	Yes				Factitious.
Clarence T. Marsh:							
Sample 1	Present		No.				Straight whisky.
2	Present		Yes				Factitious; a mixture of spirits of different ages colored up.
3	Present		Yes				Factitious; straight whisky and methyl alcohol colored up.
4	None		Yes				Factitious colored spirits not aged in wood.
McCandless, Williams, Burton:							
Sample 1	Yes	No.	No.				Genuine whisky.
2	Yes	No.	Yes				Not all genuine; probably blended with factitious whisky.
3	Yes	No.	Yes				Not genuine; contains more factitious than No. 2, also contains wood alcohol.
4	No.	Yes	Yes				Wholly factitious.
Harris E. Sawyer:							
Sample 1	Strong	No.	No.		Good	Good	Straight whisky of good quality.
2	Strong	Yes, strong	Yes		Fair	Fair	Colored somewhat; probably a blend of good quality.
3	Moderate	Yes, slight	Yes		"Split"	"Split"	Colored a little and "split" with methyl alcohol.
4	None	Yes	Yes		False	False	Entirely factitious.
R. E. Stallings:							
Sample 1	Yes		None	Good	Good	Good	Genuine.
2	Yes		Considerable.	Good	Good	Good	Obtained in market.
3	Yes		Some	Good	Good	Bad	Added methyl alcohol.
4	No.		Large amt.	Good	Bad	Bad	Not a whisky.
L. H. Van Wormer:							
Sample 1	Yes						Probably a pure whisky.
2	Yes						About half-and-half.
3	Yes						About one-quarter pure whisky.
4	No.						Entirely spurious.

TABLE I.—*Results of analyses of official samples of whiskies*—Continued.

Analyst.	Tests, etc.						Conclusions as to character of the samples analyzed.
	Tannins.	Caramel (paraldehyde).	Caramel (amyl alcohol).	Character of color.	Taste.	Odor.	
Albert E. Leach:							
Sample 1[a]							
3			Trace				Mixed whisky.
3			Trace				Whisky with methyl alcohol.
4			Considerable.				Factitious.

Analyst.	Acids.			Conclusions as to character of the samples analyzed.
	Free acids (acetic).	Combined acids.	Total acids.	
Bureau of Chemistry:	*Per cent.*	*Per cent.*	*Per cent.*	
Sample 1		0.009	0.069	Straight uncolored whisky.
2		.009	.058	Contains some whisky, but diluted with proof spirits, and colored by caramel.
3		.007	.048	Also contains whisky, but diluted with proof spirits, methyl alcohol, and colored by caramel.
4		.005	.007	Purely artificial.
Joseph A. Deghuée:				
Sample 1				Straight whisky.
2				Contains added coloring matter.
3				Contains added coloring matter and methyl alcohol.
4				Colored alcohol and not a whisky at all.
A. Lasché:				
Sample 1	0.060			
2	.050			
3	.039			
4	.008			
Leroy M. Law:				
Sample 1	.070			Straight whisky.
2	.064			Commercial.
3	.048			Commercial with methyl alcohol added.
4	.009			Factitious.
Clarence T. Marsh:				
Sample 1	.060			Straight whisky.
2	.048			Factitious; a mixture of spirits of different ages colored up.
3	.039			Factitious; straight whisky and methyl alcohol colored up.
4	.0024			Factitious colored spirits not aged in wood.
McCandless, Williams, Burton:				
Sample 1	.0432			Genuine whisky.
2	.0336			Not all genuine; probably blended with factitious whisky.
3	.0264			Not genuine; contains more factitious than No. 2, also contains wood alcohol.
4	.0018			Wholly factitious.
Harris E. Sawyer:				
Sample 1	[b]4.8	[b]4.8		Straight whisky of good quality.
2	[b]3.9	[b]4.0		Colored somewhat; probably a blend of good quality.
3	[b]2.9	[b]3.2		Colored a little and "split" with methyl alcohol.
4	[b].2	[b].3		Entirely factitious.
R. E. Stallings:				
Sample 1		[b]1.6	[b]10.1	Genuine.
2		[b]1.8	[b]8.1	Obtained in market.
3		[b]1.4	[b]7.0	Added methyl alcohol.
4		[b]1.0	[b]1.2	Not a whisky.
L. H. Van Wormer:				
Sample 1				Probably a pure whisky.
2				Almost half-and-half.
3				About one-quarter pure whisky.
4				Entirely spurious.
Albert E. Leach:				
Sample 1[a]				
2				Mixed whisky.
3				Whisky with methyl alcohol.
4				Factitious.

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[a] This sample not received.

[b] Cubic centimeters N/10 per 100 cc.

Table II shows the average of the analytical figures obtained for extract, alcohol, color removed by ether and by fuller's earth, together with the maximum variation above and below the average figure in each determination.

TABLE II.—*Average, maximum, and minimum results obtained by chemists on referee's samples of whisky.*

Data.	Average.	Highest variation.	Lowest variation.
Extract:	*Per ct.*	*Per ct.*	*Per ct.*
Sample 1	0.152	0.012	0.016
Sample 2	.198	.026	.054
Sample 3	.147	.066	.022
Sample 4	.110	.007	.006
Alcohol by weight:			
Sample 1	43.09	2.47	.57
Sample 2	42.04	.69	.79
Sample 3	41.28	2.13	.98
Sample 4	42.37	2.27	1.15

Data.	Average.	Highest variation.	Lowest variation.
Color removed by ether:	*Per ct.*	*Per ct.*	*Per ct.*
Sample 1	35.2	2.8	3.5
Sample 2	23.9	4.6	6.9
Sample 3	21.4	6.5	8.9
Sample 4	5.1	6.0	5.1
Color removed by fuller's earth:			
Sample 1	60.5	5.5	2.2
Sample 2	72.4	7.6	8.4
Sample 3	72.4	7.6	4.8
Sample 4	93.5	6.5	8.8

COMMENTS BY ANALYSTS.

J. A. Deghuée: The fusel oil was determined by the Roese method, which gave apparently satisfactory results except in the case of No. 3, the sample containing methyl alcohol. In this case the method gave a negative quantity, i. e., the reading was less than that obtained with fusel free alcohol. An attempt was made to check the results and at the same time study the relative value of the carbon tetra-chlorid method, but it was found impossible to make the connections in the apparatus absolutely tight with ordinary stoppers. A distillation apparatus with ground glass joints is necessary in order to obtain perfectly satisfactory results. Such an apparatus is being made for the laboratory, but up to the present writing has not been delivered. I hope to test the method more fully when this has been received.

Both the methyl anilin violet method and the copper spiral method were used in testing for the presence of methyl alcohol. The objection to the spiral method is of course the well-known fact that even pure ethyl alcohol will form traces of formaldehyde if the oxidation is pushed too far. The simplicity of the method, however, is greatly in its favor, and in practice, where a considerable quantity of methyl alcohol would be present if there at all, this method is perfectly reliable. There would be no object, for instance, in adulterating a liquor with a trace of methyl alcohol, and for the larger amounts used a moderate degree of oxidation with the spiral is ample for detection.

A. Lasché: All four samples were examined for methyl alcohol according to the Riche, Bardy, and Carl Windisch method, known as the official method of the German Government, with the result that sample No. 3 responds positively to this test for methyl alcohol, whereas the result with the other three samples was negative.

J. M. McCandless, R. G. Williams, and Jos. Q. Burton: Alcohol was determined by weight weighing both sample and distillate; acidity, ethers, and fusel oil by the method of Allen, by which my work last year was done, and which I described to you. The detection of wood alcohol was effected by a new method, due to Mr. J. Q. Burton, of this laboratory, and which I have not time at this writing to describe to you.

R. E. Stallings: Specific gravity was determined at 15.6° C. in a pycnometer.

Solids (extract): 100 cc was dried down and heated for two and one-half hours in a water bath at 100°, cooled, and weighed.

Alcohol: 25 cc were weighed, 100 cc of water added, and 100 cc distilled over. The distillate was not weighed. The specific gravity of distillate was determined.

Acids: Total acids were determined by taking 100 cc and titrating with tenth normal sodium hydroxid.

Fixed acids were determined by taking 100 cc, evaporating to dryness, adding 25 cc of water, and evaporating to dryness, taking up with water and titrating.

Fusel oil was determined by method found in Bulletin 65, page 96. It was found difficult to maintain the temperature at 15° C.

Fuller's earth: To 25 cc of whisky, 5 grams of fuller's earth were added and shaken every five minutes for one hour, filtered through S. & S. filter, and compared with original liquor by colorimeter.

Methyl alcohol was detected by Riche and Bardy's test.

Detection of artificial coloring matter, method of Clarence T. N. Marsh: Chloroform absorption test: 5 cc of whisky are placed in a test tube, 5 cc of chloroform added, and 10 cc of water, and shaken carefully once or twice. In sample No. 1 chloroform absorbs color; in No. 2, chloroform absorbs some color; in No. 3, both layers are colored; and in No 4, the chloroform layer is colorless, showing caramel to be in No. 3 to reenforce the color and that in No. 4 caramel was the coloring.

Subacetate of lead: A few drops of reagent were added to about 5 cc of samples in test tubes. Sample No. 1 showed an abundance of tannin, No. 2 and No. 3 became turbid, while No. 4 remained unchanged, showing no tannin. The color of the whisky was extracted with ether (qualitatively) and the amount of color removed was carefully estimated. Ether was added to each sample of the whisky, agitated, and separated. In No. 1 the ether took about 35 per cent of the color; No. 2, about 17 per cent; No. 3, about 12.5 per cent, and No. 4, about 1 per cent.

L. H. Van Wormer: Tests for methyl alcohol: In the Trillat method, on addition of lead dioxid to No. 3, the liquid turns blue in the cold. The color is not destroyed by boiling. The addition of lead dioxid to No. 4 produces a greenish yellow, changing quickly to green. On boiling, this color fades and changes to a blue; this finally changes to a dirty gray tinged with blue. No. 3 was the only one I tested by the Riche and Bardy method. Twenty-five cc of the whisky were placed in a flask with about 15 grams of potassium carbonate, and 10 cc distilled by means of a Glinski bulb tube, this 10 cc of alcohol being used in the test. On extracting with the warm alcohol a deep purple liquid was obtained which looked almost black in the 100 cc graduated. By placing a little of this solution in a porcelain dish and diluting several times with alcohol, the purple color became evident. No other samples were tested by this method. No. 3 gave a slight, rather questionable test with the copper coil test. These methods are all that can be desired from the standpoint of delicacy, but would be rather tedious in case of a large amount of work. The following shorter method is suggested for trial: Pass the alcohol vapor over heated copper oxid in a combustion tube, with the usual precautions against explosion; arrange the delivery end of the combustion tube so that it will point nearly straight downward. The aldehydes may be collected in test tubes containing a little water. If desired, the escaping gas from the delivery tube may be tested for formaldehyde. To do this, place a little sulphuric acid, on which are floating a few crystals of morphine, in a porcelain evaporating dish, and hold under the delivery tube so that the end of the tube will be only slightly above the surface of the acid. One sample, which was so dilute that the Scudder and Mulliken test failed, gave a heavy test almost immediately.

Albert E. Leach: It is impossible to determine the fusel oil by the Roese method in sample No. 3 on account of the presence of methyl alcohol. The immersion refractometer when further studied will apparently prove of considerable use in judging of the purity of distilled liquors. Methyl alcohol was detected and determined by the refractometric method of Leach and Lythgoe.[a]

Comments of Associate Referee.

The results obtained in the cooperative work on distilled liquors this year are even more satisfactory than last, in respect to the determination of the character of the samples. Notwithstanding the fact that the problem was purposely made more difficult in the samples chosen (Nos. 2 and 3 both contain a large proportion of genuine whisky), the analysts were able (with the exception of one analyst who did not think his results justified positive conclusions) to arrive at correct conclusions concerning them.

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[a] J. Am. Chem. Soc., 1905, *27:* 964.

The results are also highly satisfactory as regards the detection of the presence of methyl alcohol. Not only was qualitative proof of its presence in sample No. 3 obtained by every analyst, but several very close quantitative determinations were made of the amount present, an achievement made possible by the application of the immersion refractometer to the estimation of mixtures of ethyl and methyl alcohol by Leach and Lythgoe. This method was published after the samples had been sent out, but Doctor Leach kindly offered to apply it to the samples, and it was called to the attention of several other collaborating analysts. With this method of exact estimation, and with such satisfactory tests as the Trillat and the Riche and Bardy's, there should be no difficulty in the future in dealing with this very dangerous addition.

The only method for this determination given in the provisional methods of the association (under the head of flavoring extracts) is that of Scudder and Mulliken, oxidation with copper spiral, a method which is decidedly unsatisfactory and unreliable, nothwithstanding its adoption by the pharmacopœial revision committee.

Coming to the comparison of analytical results, there is less cause for congratulation. The color absorption figures are decidedly better than last years'; in fact, the variations are small in consideration of all the difficulties inherent in the methods. The value and reliability of the color absorption methods for detecting the presence of artificial coloring matter are fully demonstrated. The alcohol results are again unsatisfactory, being even more divergent than last year's. The referee is unable to account for this, and can only hope that with greater care in manipulation and closer attention to details of analysis by collaborating chemists, better results can be obtained in the future. It is not believed that the difficulty lies with the method prescribed for this estimation, as it has been in use for many years, and has given satisfactory results in careful hands.

The Marsh test for the presence of artificial coloring, using amyl alcohol as a selective solvent for the natural coloring matter derived from wood, was found to give satisfactory results and will doubtless be a valuable addition to the tests already in use. It is used to a considerable extent as a field test by internal-revenue officers.

Nearly all of the analysts reported figures for fusel oil this year, and the results, while very divergent, are really better than the writer expected. Several discarded entirely the official method and used the Allen-Marquardt, or individual modifications of it, and their results could not be expected to compare with the rest. The difficulties in the way of securing agreeing results on this determination were pointed out in my report last year, and can only be overcome by a rigid adherence to a prescribed method and a closer study and elimination of its sources of error.

The work this year has demonstrated that fusel oil can not be determined by the Roese method in the presence of methyl alcohol. A few analysts report small quantities present in sample No. 3, but most of them reported negatively.

Two of the collaborators, Doctors Lasché and Sawyer, made a special study of fusel oil methods. The former has sent in a report containing valuable conclusions as to the results of his observations, with a number of recommendations concerning the details of the Roese method, a resumé of which is appended.

Special Study of Fusel Oil Determinations, by A. Lasché.

Different methods for the determination of fusel oil or amyl alcohol in spirits were investigated, and especially Schidrowitz's modification of the Allen-Marquardt method as described in the directions which were sent by Doctor Wiley to collaborators. The method is also described in Vasey's Analyses of Potable Spirits. I find this method to be inaccurate and impracticable, and anything but an improvement over the Roese method. Ernst Beckmann has published a modification of his old method in the Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.[a] He has very much simplified his method and it seemed to the writer that by means of this method the natural error of the Roese method should be reduced. The result, however, was not what was expected and the source of error is considerably greater than is inherent in the Roese method.

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[a] July 15, 1905, p. 143.

Beckmann himself states that the Roese method is simpler. The error with the Beckmann method amounts to from 10 to 30 per cent of the amount of fusel oil or amyl alcohol contained. The maximum error inherent in the Roese method for different proofs of whisky is expressed by the following figures:

Proof.	Fusel oil error (per cent).
70	0.0232
90	.0265
100	.0330
110	.0365
150	.0497
170	.0563
190	.0629

A slight alteration in the method as described in Bulletin No. 65, page 96, is suggested, otherwise the method of procedure and calculation is in accordance with the method used in our laboratory, and which gives very satisfactory results. We make 200 or more fusel oil determinations every year, and many determinations have been checked with the result that the error was less than 10 per cent in the amount of fusel oil contained at 100 proof.

Our modus operandi is as follows: Measure off exactly 200 cc of the whisky at 15.5° C. Pour into the distilling flask and rinse the measuring flask with 25 cc. of distilled water and add to the distilling flask. Now add 3 cc. normal soda or potash solution and distill rapidly over direct flame until 190 cc. have distilled over. Fill the distillate up to 200 cc with distilled water at exactly 15.5° C. and from now on follow the description as given on page 97 in Bul. 65, using, however, 15.5° C., wherever 15° C. is stated. In calculating fusel oil the factor 0.6631 is used in place of 0.663.

In the writer's opinion the association should continue to recommend the Roese method, since it is certainly the most practical of the methods which have been suggested. It was discovered within the last few months that some analysts are making great errors in reporting fusel oil determinations. For instance, reports are being sent out by one large concern reporting the analyses, as follows:

	Sample No. 1 (per cent).
Amyl alcohol, by volume	0.19
Fusel oil, by weight	.78

They stated, in answers to questions which were sent them, that such a report gives the amount of fusel oil and amyl alcohol contained in the samples as submitted. They are using the Roese method, and state that the percentage of amyl alcohol and fusel oil were determined according to the tables to be found in Dr. J. Koenig's book, "Die Untersuchung landwirthschaftlich und gewerblich wichtiger Stoffe," second edition, pages 500–504, inclusive.

The first table given in this work is the same as that on page 132 of "Arbeiten aus dem Kaiserlichen Gesundheitsamt," vol. 4 (Sell). This table can not be used, and it is not intended that it should be used for obtaining the percentage of fusel oil according to the method described. The second table contained in Koenig's book is one which is supposed to give the percentage of fusel oil figured to absolute alcohol. The chemists above referred to get their amylic alcohol by volume per cent from the first table and then refer to the second table and get the fusel oil by weight. The second table in Koenig's book holds good only in case 100 cc of the whisky are distilled and reduced to 30 per cent by volume, and if the original sample of whisky contains exactly 50 per cent by volume of alcohol.

The attention of chemists is called to the incorrectness of these tables and they are advised to calculate the percentage of fusel oil or amylic alcohol (both terms being synonymous in using the Roese method), as directed in Bulletin 65.

The table in Lehmann's "Die Methoden der praktischen Hygiene," second edition, page 529, is useless. It is like Table 1 in Koenig's book. The table in Elsner's "Die Praxis des Chemikers" on page 400 is correct. It is the original table worked out by Sell.[a] Maercker-Delbrueck, eighth edition, page 208, "Methods of calculation" is correct, but I do not concur in figuring fusel oil to absolute alcohol in a sample. Such a basis would be theoretically incorrect.

Dr. Geo. Lunge [b] also calculates fusel oil to a basis of absolute alcohol and from these recent editions of German works, it appears that this is now the basis of calculation of fusel oil in liquors in Germany.

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[a] Arbeiten des Kaiserlichen Gesundheitsamt, *4:* 137.

[b] Chemisch-technische Untersuchungsmethoden, 5th ed., *3:* 579.

It is the writer's opinion that fusel oil should be reported calculated to 100 U. S. proof spirits and not as contained in the sample submitted, because whisky as consumed has approximately this proof. It certainly is not correct to report a whisky, for instance, an old Maryland rye, having 170 proof as containing 0.5 per cent of fusel oil. This whisky reduced to 100 would only have 0.29 per cent of fusel oil.

LITERATURE.

Literature of this subject, 1905.

Author.	Publication.	Reference.
Beckmann	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.	July 15, 1905.
Koenig	Die Untersuchung landwirthschaftlich und gewerblich wichtiger Stoffe.	2d ed., pp. 500 to 504, inclusive.
Sell	Arbeiten aus dem Kaiserlichen Gesundheitsamt	Vol. 4.
Lehmann	Die Methoden der praktischen Hygiene	2d ed., p. 529.
Elsner	Die Praxis des Chemikers	P. 400.
Maercker-Delbrueck	Methods of Calculation	8th ed., p. 208.
Lunge	Chemisch- technische Untersuchungsmethoden	5th ed., *3:* 579.
Leach and Lythgoe	The Detection and Determination of Ethyl and Methyl Alcohols in mixtures by the Immersion Refractometer.	J. Amer. Chem. Soc., *27:* 964.

RECOMMENDATIONS.

It is recommended that—

(1) The Trillat[a] test for the detection of methyl alcohol in distilled liquors, as follows be made a provisional method:

To 50 cc of spirit add 50 cc of water and 8 grams of lime, and fractionally distill by the aid of Glinski bulb-tubes. The first 15 cc of the distillate are then diluted to 150 cc, mixed with 15 grams of potassium bichromate and 70 cc of sulphuric acid (1:5), and left for one hour, being shaken at intervals.

This liquid is then distilled, the first 25 cc being rejected and distillation stopped when 100 cc have been collected.

Fifty cc of distillate are mixed with 1 cc of rectified dimethyl-anilin, transferred to a stout, tightly-stoppered flask, and kept on bath at 70° to 80° C., for three hours, with occasional shaking.

The liquid is then rendered distinctly alkaline with sodium hydroxid and the excess of dimethyl-anilin distilled off, distillation being stopped when 25 cc have passed over.

Residue in flask is acidified with acetic acid and shaken, and a few cubic centimeters tested by adding 4 or 5 drops of water with lead dioxid in suspension (1 gram in 100 cc). If methyl alcohol be present, a blue coloration occurs and is further developed by boiling.

NOTE.—Ethyl alcohol thus treated yields a blue coloration changing immediately to green, afterwards to yellow, and becoming colorless when boiled.

(2) That the Riche and Bardy test[b] for the detection of methyl alcohol in distilled liquors, as follows, be made a provisional method.

The following process has been devised by MM. Riche and Bardy for the detection of methyl alcohol in commercial spirit of wine. It depends on the formation of methyl anilin violet:

Ten cc of the sample of alcohol, previously rectified, if necessary, over potassium carbonate, are placed in a small flask with 15 grams of iodin and 2 grams of red phosphorus. Methyl and ethyl iodids are formed and should be distilled off into about 30 cc of water. The heavy, oily liquid which settles to the bottom is separated from the water and transferred to a flask containing 5 cc of anilin. The flask should be placed in cold water in case the action should be violent; or, if necessary, the reaction may be stimulated by gently warming the flask. After one hour the product is boiled with water and solution of soda added, when the bases rise to the top as an oily layer, which may be drawn off with a pipette after filling the flask with water up to the neck. One cc of the oily liquid thus obtained is next oxidized by adding to it 10 grams of a mixture of 100 parts of clean sand, 2 of common salt, and 3 of cupric nitrate. After being thoroughly mixed the whole is introduced into a glass tube and heated to 90° C. for eight or ten hours. The product is exhausted with warm alcohol, the liquid filtered, and made up with alcohol to 100 cc. If the sample of spirit be pure, the tint of the liquid is red, but in the presence of 1 per cent of methyl alcohol it has a distinct violet shade; with 2.5 per cent the shade is very distinct, and still more so with 5 per cent. To detect more minute quantities of methyl alcohol 5 cc of the colored liquid are diluted to 100 cc with water and 5 cc of this again diluted to 400 cc. The liquid thus obtained is heated in porcelain and a fragment of white merino (free from sulphur) immersed in it for half an hour. If the alcohol be pure, the wool will remain white, but if methylated the fiber will become violet, the depth of tint giving a fair approximate indication of the proportion of methyl alcohol present.

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[a] Analyst, 1899, *24:* 13, 211, 212.

[b] Allen's Commercial Organic Analysis, 3d ed., *1:* 80.

(3) That the method of Leach and Lythgoe for the estimation of ethyl and methyl alcohol in mixtures of the same be made provisional. This method is modified for different liquors, and the following is more specifically for whiskies:

Fifty cc of the sample are weighed and mixed with 75 cc of water and 100 cc distilled off. The distillate is weighed, specific gravity taken, and calculation of total alcohols made for weight of sample, using ethyl alcohol tables. The distillate is then examined by the immersion refractometer and the reading corrected to 20° C., using per cent alcohol by weight (as total alcohol). Find from Table II [a] the scale reading for ethyl and methyl alcohol corresponding to the per cent of alcohol, by weight, determined by specific gravity, and calculate as follows:

(Reading for ethyl)$-$(Reading of distillate)$=X$.

$X\div$(difference between ethyl and methyl readings) 100=per cent of the alcohol present which is methyl.

Then calculate to weight or volume in original sample.

(4) That the following method for the determination of ethereal salts be substituted for the method given in Bulletin 65, page 98:

In 50 cc of the distillate neutralize the free acid with N/10 alkali, using phenolphthalein as an indicator, then add 25 cc N/10 alkali and either heat for one hour with a reflux condenser, cool and titrate with N/10 acid, or allow the solution to stand overnight in a stoppered flask with the excess of alkali, then heat with a reflux condenser for one-half hour at a low temperature, cool and titrate. The number of cubic centimeters of N/10 alkali used in the saponification of the esters is calculated as ethyl acetate.

The distillate of esters, aldehydes, and furfurol is prepared in the following manner: Add 25 cc of water to 200 cc of the whisky and distill until 200 cc are distilled off. It is advisable to use a mercury valve in order to prevent loss of alcohol, and the distillation should be made slowly.

(5) That the following method for the determination of aldehydes be substituted for the method given in Bulletin 65, page 97:

Determine the aldehydes in the distillate prepared for the esters. Five to 10 cc of the distillate are diluted to 50 cc with aldehyde-free alcohol (50 per cent by volume), 25 cc of the reagent added, and allowed to stand for twenty minutes at 15° C. The solutions and the reagents should be at 15° C. before they are mixed.

Reagent.—Dissolve 0.5 gram of pure fuchsin in 500 cc of water, then add a water solution of sulphur dioxid, equivalent to 5 grams of sulphur dioxid, and make the whole up to 1 liter. This solution can be used as soon as it becomes colorless and will keep for several days.

Aldehyde-free alcohol is prepared by treating ordinary 95 per cent alcohol with potassium hydroxid and distilling. Then this distillate is treated with about 3 grams to the liter of metaphenelenediamin hydrochlorate and heated with a reflux condenser for several hours, then distilled slowly, not keeping the first 100 cc nor the last 100 cc. This will give an alcohol which will give only the slightest tinge of color when treated with the reagent.

The standard aldehyde solution is treated in the same way as the distillate, and the color of the standard must be very close to the color of the sample.

(6) That the following method for the determination of furfurol be substituted for the method given in Bulletin 65, page 98:

From 10 to 20 cc of the distillate are diluted to 50 cc with furfurol-free alcohol (50 per cent by volume). To this add 2 cc of colorless anilin one-half cubic centimeter of hydrochloric acid (sp. gr., 1.125) and keep for fifteen minutes in a water bath at about 15° C.

Prepare standards of known strength in the same way.

(7) That the following method for fusel oil be given a trial by the association:

To 100 cc of whisky add 20 cc of N/2 sodium hydroxid, and then saponify the mixture by boiling for one hour under a reflux condenser.

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[a] J. Amer. Chem. Soc., 1905, *27:* 969.

The flasks are connected with a distilling apparatus and 90 cc distilled over, 25 cc of water added, and the distillation continued until 25 cc more come over.

To this distillate is added as much finely ground salt as it will readily dissolve and then saturated salt solution until the specific gravity reaches 1.10. The volume at this point is not much in excess of 200 cc.

The brine solution is extracted four times with carbon tetrachlorid, using 40, 30, 20, and 10 cc, and the carbon tetrachlorid washed three times with 50 cc of saturated salt solution. It is then run into a flask containing 1 cc of sulphuric acid, 10 cc of water, and 5 grams of potassium dichromate and boiled for eight hours under a reflux condenser.

When the oxidation is complete the flask is attached to the distilling apparatus after the addition of 30 cc of water and the contents distilled until but 20 cc remain. Eighty cc more of water are then added and the distillation continued until but 5 cc are left. The distillate is neutralized to methyl orange and titrated with phenolphthalein, each cubic centimeter of N/10 sodium hydroxid equaling 0.0088 gram of amyl alcohol.

Notes.—Rubber stoppers can be used in the saponification and first distillation, but corks covered with tinfoil must be used in the oxidation and second distillation. Corks and tinfoil must be renewed frequently.

Instead of the saponification as given, the 100 cc of liquor may be allowed to stand over night on 20 cc of N/2 sodium hydroxid, and then distilled directly.

It is important to have the specific gravity of the mixture of brine and alcoholic distillate up to 1.10.

It is very difficult to make good joints where corks are covered with tinfoil, and it is a good plan to mark the height of the liquor on the flask in order to note any loss.

Carbon tetrachlorid must be purified by oxidation over acid bichromate for several hours with distillation and redistillation over barium carbonate.

(8) That the following test be tried for artificial coloring matter in whisky:

Color insoluble in water.—Evaporate 50 cc of whisky to dryness on steam bath. Add a small amount of hot water to residue, filter through a small paper into a 50 cc flask, wash out all soluble color with water, using less than 25 cc, add 25 cc 95 per cent alcohol, cool, fill to mark, and mix. Compare the color with that of original whisky and record results in per cent color lost. The character of the residue left on evaporation both before and after adding water should be carefully noted.

[The laboratory of the U. S. Department of Agriculture has just completed the analysis of a large number of distilled liquors obtained from various sources, and has had, therefore, an extensive experience with methods of analysis. As the results of their observations recommendations 4–8 for changes in existing methods are made by Mr. Tolman, and I submit the same for consideration.]

(9) That for the next year's work the referee make a further study of tests for artificial coloring matter and of the determination of fusel oil.

Mr. Sawyer stated that in his opinion a choice between the Allen-Marquardt, Beckmann, and Roese methods for the determination of fusel oil was only a choice of evils. Mr. Chace called attention to the 2,000 determinations of higher alcohols made in the Bureau of Chemistry recently, preliminary to which the most important standard methods were thoroughly tested with the result that the Allen-Marquardt process was found to be the only one yielding concordant and accurate results. It is believed that the modification recommended by Schidrowitz of distilling in a current of steam should be used when over 0.2 per cent of fusel oil by weight is present. Mr. Dubois stated that trials of the Roese method showed that the use of apparatus furnished with a stopcock was inadmissible, because of unavoidable leakage, and a return to the old apparatus without stopcocks was necessary. Other difficulties must be contended with, and after a number of comparisons it was entirely discarded.

Mr. Tolman confirmed Mr. Chace's remarks on the comparison of methods and the strictly comparable results given by the Allen-Marquardt method, and called the attention of the association to the methods at present in use for the determination of esters, by which not only the esters, but practically all of the residue was saponified. The speaker recommended that the method as given in 1903 be changed.

Mr. Tolman also called attention to the method for aldehydes as described in Bulletin 65, making the statement that the method was not clearly stated and that the solution as given is entirely too sensitive, and should be made stronger—5 grams of SO_2 instead of 0.5 gram; further, that the determination should be made at 15 degrees. The same remarks in regard to a constant temperature apply to the determination of furfurol. Recommendations in regard to these points were submitted to Committee C by the speaker.

Mr. Wiley called attention to the importance of methods for the examination of distilled liquors now occupying the attention of the whole chemical world, and said that it seemed probable that the different kinds of distilled liquors used as beverages may be divided into distinct classes as the result of chemical analysis, further calling attention to the methods now used in Great Britain by the excise officers in supervising the production of distilled liquors and preparing them for export.

Mr. Crampton spoke of the use of fuller's earth in detecting artificial color, and stated that the objection that it varies in quality can be overcome by securing it in large quantities, previously testing samples. The determination of coloring matter is not only of the greatest interest but also of the highest value in classification, and the tests with fuller's earth can be made so simple as to be used with effect by the revenue officers in the field. One sample of coloring matter was received which was put out by the manufacturer at $10 a pound with the guarantee that it would resist all known methods of detection. It was easily detected, however, proving to be a mixture of anilin dyes, red and yellow.

ARTIFICIAL COLORING MATTER IN WHISKY.

By Percy H. Walker and J. H. A. Schreiber.

During an examination of a large number of samples of whisky for artificial coloring matter a comparison was made of a number of methods.

Amthor's paraldehyde test was found so very unsatisfactory that its use was soon abandoned. Crampton and Simons's fuller's earth test,[a] though better than the paraldehyde test, has the very serious disadvantage that the fuller's earth varies so in power of absorption that results can in no way be duplicated if once the supply of fuller's earth used be exhausted. As we wished our results to be comparable throughout the whole series of analyses, and were unable at best to get as satisfactory results by this method as by others, it was also abandoned. Crampton and Simons's ether extraction test [a] is much more satisfactory than either of the above, and in a somewhat modified form was used continuously.

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[a] J. Amer. Chem. Soc., 1899, *21:* 355.

A. Lasché [b] has pointed out that much of the natural coloring matter of whisky is removed by shaking with chloroform, while caramel is not removed. C. T. N. Marsh has observed that amyl alcohol also has the property of removing the natural coloring matter and not the caramel.

L. S. Munson suggested if the ether extraction test be modified by filtering the liquid from which the alcohol has been evaporated before adding the known volume of alcohol, the loss of color is greater than when the method described by Crampton and Simons is followed exactly. This observation suggested that the use of ether might be entirely avoided, but as it was important that this point be carefully considered, tests Nos. 2 and 3 were used together instead of Crampton and Simons's method.

The following tests were finally adopted:

1. *Color removed by chloroform.*—Mix 10 cc of whisky and 10 cc of chloroform in a stoppered cylinder. Add 20 cc of water and shake well. Let stand for a few minutes to allow most of the chloroform to settle, filter through a dry paper without pouring the chloroform on the paper, and compare depth of color with that of the original whisky diluted with twice its volume of water. Express in percentage the loss of color.
2. *Color insoluble in water.*—Evaporate 50 cc of whisky to dryness on steam bath, add a small amount of hot water to the residue, filter through a small paper into a 50 cc flask, wash out soluble color, using less than 25 cc of water, add 25 cc of 95 per cent alcohol, cool, fill to mark, mix, and compare color with that of original whisky. Express result in per cent of color lost.
3. *Color insoluble in water+color extracted by ether.*—Transfer the solution prepared for test No. 2 to a separatory funnel, add 100 cc of ether and shake well, allow to settle, draw off the aqueous layer into a 50 cc flask, and wash out the last portion by pouring a little water through the ether without shaking. Fill flask to mark, mix, and compare color with that of the original whisky. Express result in per cent of color lost.
4. *Amyl alcohol test.*—To 3 cc of whiskey in a test tube add 1 cc of water and 6 cc of amyl alcohol. Shake the mixture and allow to settle. The aqueous layer remains more or less colored, depending on the amount of added coloring matter, pure whiskies giving little or no color.
5. *Character of solid matter.*—From the appearance of the residue obtained in test No. 2, both before adding water and after washing, a very good idea of the character of the whisky, as far as coloring matter is concerned, can be formed.
6. *Iron alum test.*—To 10 cc of whisky add 0.5 cc of a 1 per cent solution of iron alum. Note change.
7. *Lead subacetate test.*—To 10 cc of whisky in a graduated tube add 1 cc of lead subacetate solution, mix, and whirl in a high-speed centrifugal for five minutes. Note amount of precipitate.

Test No. 1 removes from pure whisky over 50 per cent of the coloring matter. Of 101 samples of pure rye whisky the minimum removed was 36 per cent, the maximum 75 per cent, and the average was 61 per cent. Of 114 samples of pure bourbon whisky the minimum removed was 39 per cent, the maximum 74 per cent, and the average 60 per cent. From 156 samples of whisky containing added coloring matter an average of 28 per cent was removed. This test is quick and is generally of value with deeply colored whiskies, but with pale whiskies the readings with the colorimeter are very hard to make and the test loses much of its value.

Test No. 2 is, in our opinion, one of the best tests we have. Fifty samples of pure rye whisky gave a minimum of 46 per cent, a maximum of 83 per cent, and an average of 64 per cent. Seventy-three samples of pure bourbon whisky gave a minimum of 33 per cent, a maximum of 83 per cent, and an average of 58 per cent. From 154 samples of whisky containing added coloring matter an average of 11 per cent was removed.

Test No. 3 has little value when test No. 2 is used. Of the 50 samples of pure rye whisky tested by No. 2, 49 were tested by No. 3 and gave a minimum of 52 per cent, a maximum of 84 per cent, and an average of 69 per cent. The 73 samples of bourbon and the 154 samples of artificially colored whiskies gave similar slight differences from the results of test No. 2, the average results for the pure bourbon being 64 per cent and for the artificially colored samples 14 per cent. These results show that test No. 2 gives practically all the information that can be obtained by using ether, and the use of this expensive reagent can be entirely omitted.

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[a] J. Amer. Chem. Soc., 1900, *22:* 810.

[b] U. S. Dept. Agr., Bureau of Chemistry, Bul. 90, p. 32.

Test No. 4, while not applied in a manner to get any standard set of figures for pure and adulterated whiskies, is a valuable one, as it offers a means of confirming the conclusions reached by other tests.

Test No. 5 is an excellent one and is applied at the time No. 2 is performed. It is rather difficult to describe the characteristic appearance of the solid matter, but that obtained from pure aged whisky suggests a resin and sticks to the dish after adding the water, while that from artificially colored whiskies often looks like a thick sirup and nearly all separates from the dish on adding water.

Test No. 6 is only of value in connection with other tests. The precipitate produced is generally green, sometimes blue, and of widely varying depth. Many whiskies that appear normal by this test show by other tests large amounts of added coloring matter.

Test No. 7 was found to be of no use. The character and amount of precipitate formed varies so much that no conclusions can be formed as to coloring matter in whisky from this test.

REPORT OF THE COMMITTEE ON NOMINATIONS.

For president, Mr. C. G. Hopkins, of Urbana, Ill.; for vice-president, Mr. John P. Street, of New Brunswick, N. J.; for secretary, Mr. H. W. Wiley, of Washington, D. C.; as additional members of the executive committee, Mr. Harry Snyder, of St. Anthony Park, Minn., and Mr. M. B. Hardin, of Clemson College, S. C.

Wm. Frear,
B. F. Kilgore.
R. J. Davidson.

The nominations were confirmed, and the president declared the gentlemen named elected for the ensuing year.

SECOND DAY.

FRIDAY—MORNING SESSION.

At the opening of the morning session the reports of the associate referees on food adulteration were continued, as follows:

REPORT ON FLAVORING EXTRACTS.

By E. M. Chace, *Associate Referee.*

The referee regrets that no satisfactory work upon flavoring extracts has been done during the past year. Only one chemist offered to collaborate, and the time which the referee could give to the subject has been very limited.

The work had been outlined as follows:

(1) Comparison of the two following methods for the determination of vanillin with the method adopted by the association: (1) Winton and Bailey's modification of the Hess and Prescott method, giving opportunity for the determination of acetanilid if present; and (2) the bromin colorimetric method.

(2) A thorough test of the present methods for the determination of citral in oil of lemon.

(3) An application of the immersion refractometer for the determination of methyl alcohol as suggested by Leach.

It is suggested that work might also be carried on to advantage along the following lines:

(1) Application to extracts of the methods for the detection of caramel as applied to whiskies.

(2) Application of a method for measuring the purity of extracts by means of the volume of their lead acetate precipitate.

(3) Effect of the presence of glycerin on the precipitation of the resins.

(4) Study of the crystalline forms of vanillin and coumarin.

REPORT ON FATS AND OILS.

By L. M. Tolman, *Associate Referee.*

Titer Test.

The cooperative work on the titer test was continued this year. Circular No. 22, Bureau of Chemistry, was issued early in the year, giving a review of the work done and suggesting a method. This method has been subjected to criticism and trial this year and, with a few minor changes, will be recommended as a provisional method. As was shown by the work of last year, the chief difference of opinion was as to the method to be used for drying the fatty acids. This has been the chief work of the year, with the result that a large majority of the workers are agreed that the two methods of drying give the same results.

A meeting of a large number of the chemists interested was held in Chicago in August, and, as a result of that meeting, it was decided to recommend the following method for adoption by the association as provisional, and that further study be made of the method of drying the fatty acids during the coming year.

METHOD.

Weigh 75 grams of fat into a metal dish and saponify by using 60 cc of 30 per cent sodium hydrate (36° Baumé caustic soda) and 75 cc of 95 per cent by volume alcohol, or 120 cc of water. Boil down to dryness, with constant stirring, to prevent scorching. This should be done over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and, if alcohol has been used, boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc of 30 per cent sulphuric acid (25° Baumé sulphuric acid) to free the fatty acids, and boil until they form a clear, transparent layer and wash with boiling water until free from sulphuric acid. Collect the fatty acids in a small beaker and place on the steam bath until the water has settled and the fatty acids are clear, then decant them into a dry beaker, filter, using a hot-water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° C. or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm in diameter and 100 mm in length (1 by 4 inches) and made of glass about 1 mm in thickness. This is placed in a 16-ounce, salt-mouth bottle of clear glass, about 70 mm in diameter and 150 mm high (2⅘ by 6 inches), fitted with a cork, which is perforated so as to hold the tube rigidly when in position. The thermometer, graduated to 0.1° C., is suspended so that it can be used as a stirrer, and the mass is stirred slowly until the mercury remains stationary for thirty seconds. The thermometer is then allowed to hang quietly, with the bulb in the center of the mass, and the rise of the mercury observed. The highest point to which it rises is taken as the titer of the fatty acids.

The fatty acids are tested for complete saponification as follows: Three cc of the fatty acids are placed in a test tube and 15 cc of alcohol (95 per cent by volume) added. The mixture is brought to a boil and an equal volume of ammonia (0.96 sp. gr.) added. A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

STANDARD THERMOMETER.

The question of a standard thermometer was also taken up this year and the question was submitted to the different collaborators. After the suggestions from these had been received the referee discussed the matter with C. W. Waidner, of the Bureau of Standards, and recommends the following for adoption as the standard thermometer for the titer test:

Thermometer is graduated in one-tenth degrees, from 10°–60°, with a zero mark, and has an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm below the 10° mark. The 10° mark is about 3 or 4 cm above the bulb, the length of the thermometer being about 15 inches over all. The bulb is of Jena normal 16^{III} glass and the thermometer annealed for seventy-five hours at 450° C. The bulb is of moderately thin glass so that the thermometer will be quick acting, the bulb being about 3 cm long and 6 mm in diameter. The stem of the thermometer is 6 mm in diameter and made of the best thermometer tubing with scale etched on the stem. The graduation must be clear-cut and distinct but quite fine. The thermometer should be furnished with a felt-lined case.

Cold Test.

At the request of a number of chemists interested, a study of the "cold test" was undertaken this year. Preliminary to undertaking any work, an effort was made to collect all the methods in use, and a circular was issued on June 17, 1905, giving all the methods having any general use. The following are the methods classified under the name of the "cold test:"

PRUSSIAN RAILWAY METHOD.

The sample, freed from water and mechanical impurities, is introduced in a U tube of 6 mm internal diameter (two tubes are shown in Fig. 1). This is immersed in a vessel *h*, filled with the freezing mixture of the specified temperature, and surrounded by vessel *i*, which is also filled with the freezing mixture. The temperature is controlled by a thermometer. The U tube should stand at least one hour without being disturbed in the freezing mixture, the level of the oil being about 10 mm below that of the freezing mixture. The tube is then carefully drawn out so far that the level can be observed when the india-rubber tube *d* is slipped over its end while pinch-cock *e* is open. Close *e*, and by opening pinch-cock *f*, allow a pressure of 50 mm (generated by pouring water into vessel *a*, in which the weighted funnel *b* is placed, and controlled exactly by manometer *c*) to act on the oil.

According to the rules of the Prussian State Railway direction "winter oil" must remain fluid at —15° C. and "summer oil" at — 5° C. This is considered to be the case when the oil, cooled to −15° C. or −5° C., as the case may be, and subjected to the constant pressure of a water column of 50 mm, will rise in the glass tube of 6 mm internal diameter at the minimum rate of 10 mm per minute.

COLD TEST, FROM UNITED STATES NAVY SPECIFICATIONS.

A couple of ounces of oil is put in a 4-ounce sample bottle, and a thermometer placed in it. The oil is then frozen, a freezing mixture of ice and salt being used if necessary. When the oil has become hard the bottle is removed from the freezing mixture and the frozen oil allowed to soften, being stirred and thoroughly mixed at the same time by means of the thermometer until the mass will run from one end of the bottle to the other. The reading of the thermometer, when this is the case, is regarded as the cold test of the oil.

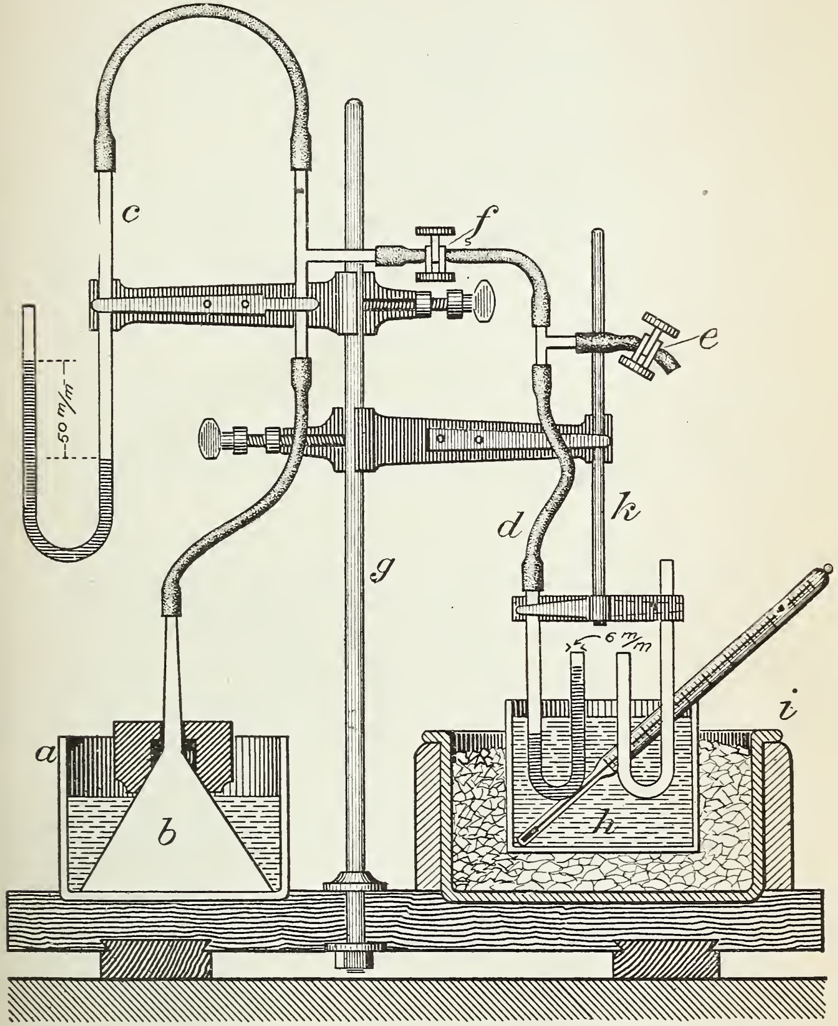

Fig. 1.—The Prussian State Railway official apparatus for the cold test (Lewkowitsch).

COLD TEST OR CLOUD TEST AS USED IN THE LABORATORIES OF ARMOUR & CO.

The method of making the cold test as used in the Armour laboratories varies according to the character of the oil to be tested. The clouding test is used exclusively, and where this test is employed certain conditions must be fulfilled:

(1) The oil must be perfectly dry, because the presence of moisture will produce a turbidity before the clouding point is reached.

(2) The oil must be heated to 150° C. over a free flame immediately before making the test.

(3) There must not be too much discrepancy between the temperature of the bath and the clouding point of the oil. An oil that will cloud at the temperature of hydrant water should be tested in a bath of that temperature. An oil that will cloud in a mixture of ice and water should be tested in such a bath. An oil that will not cloud in a bath of ice and water must be tested in a bath of salt, ice, and water.

The test is conducted as follows: The oil is heated in a porcelain casserole over a free flame to 150° C., stirring with the thermometer. As soon as it can be done with safety the oil is transferred to a 4-ounce oil bottle, which must be perfectly dry. One and one-half ounces of the oil is sufficient for the test. A dry Fahrenheit thermometer is placed in the oil and the bottle is then cooled by immersion in a suitable bath. The oil is constantly stirred with the thermometer, taking care not to remove the thermometer from the oil at any time during the test, so as to avoid stirring air bubbles into the oil. The bottle is frequently removed from the bath for a few moments. The oil must not be allowed to chill on the sides and bottom of the bottle. This is effected by constant and vigorous stirring with the thermometer. As soon as the first permanent cloud shows in the body of the oil, the temperature at which this cloud occurs is noted.

With care results concordant to within 1° F. can be obtained by this method. The Fahrenheit thermometer is used merely because it has become customary to report results in degrees Fahrenheit.

The oil must be tested within a short time after heating to 150° C., and a retest must always be preceded by a reheating to that temperature. The cloud point should be approached as quickly as possible, yet not so fast that the oil is frozen on the sides or bottom of the bottle before the cloud test is reached.

COLD TEST FOR LARD OIL, AS PRESENTED BY THE NEW YORK PRODUCE EXCHANGE.[a]

The oil to be tested shall be taken from at least one-quarter of the barrels sold or delivered and when well mixed together shall be placed in a glass bottle, such as is now used to test the specific gravity of paraffin and other oils, which bottle shall not be over 4 nor under 2 inches in diameter nor over 10 nor under 6 inches in height. The thermometer shall be placed in the oil, and when it indicates the degree at which the test is to be made it must not be allowed to go more than 1 degree below nor 1 degree above that point. After remaining four hours, if the oil shows no evidence of congealing, it shall constitute a good delivery.

COLD TEST AS USED BY NELSON MORRIS & CO.

Approximately 50 cc of the oil to be tested are placed in a 4-ounce oil bottle, and the bottle and contents put in a freezer and allowed to remain there until the oil is frozen solid. The temperature of our freezer is about −5° to 0° F. A freezing mixture will answer the purpose.

The bottle is then placed in an ice box, temperature about 40° F., for about fifteen minutes, in order to allow the oil to soften somewhat. Then a stout glass rod is inserted, the lumps broken up, and the oil well stirred until it becomes homogeneous throughout. Then the glass stirring rod is replaced by a delicate Fahrenheit thermometer graduated to fifths of 1 degree, and the stirring continued until the oil will flow from one end of the bottle to the other. The reading of the thermometer at this point is taken as the cold test of the oil.

In the case of oils of low cold test, such as winter-pressed neat's-foot oil, we make the test as soon as the oil is brought from the freezer. In the case of oils having a cold test of 40° F. or over, we allow them to soften for fifteen minutes in the ice box. The cold tests that we make on animal oils cover a range of from 20° F. to 70° F.

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[a] Report N. Y. Produce Exchange, 1902, p. 262.

COLD TEST AS USED BY THE CENTRAL LARD COMPANY.

Two ounces of the oil are placed in an ordinary 4-ounce oil bottle and allowed to stand in a temperature below 40° F. for at least twenty-four hours. In this laboratory the refrigerator used for such purposes has a mean temperature of —5° C. The solidified oil is then broken up and stirred with a heavy stirring rod until it reaches such a consistency that the thermometer may be introduced and used instead. Then it is stirred and manipulated until the oil will flow from one end of the bottle to the other with no apparent lumpiness. The temperature shown at this moment is taken as the cold test.

COLD TEST AS USED BY THE CUDAHY PACKING COMPANY.

Put about 100 grams of oil in a 4-ounce oil sample bottle and place this in a bath for six hours The bath is to be maintained at the temperature the oil is guaranteed to stand. If the oil will run in the bottle at the end of this time, it will be considered to stand the test even though some solid matter may have separated.

COLD TEST AS USED BY SCHWARZSCHILD & SULZBERGER.

A test tube 6 inches by 1 inch is filled 1 inch high with the melted fat or oil, a thermometer fitted with a cork is inserted and the test tube placed in a freezing mixture of salt and ice When the oil begins to solidify take out and stir with the thermometer. Again place the test tube in the freezing mixture and while holding keep on stirring with the thermometer to obtain a homogeneous mass. When the oil just flows evenly down the side of the test tube, read the temperature.

COLD TEST FOR WINTER COTTON OIL, AS PRESENTED BY THE NEW YORK PRODUCE EXCHANGE.[a]

A regular 4-ounce sample bottle shall be filled full of oil to be tested, a thermometer shall be inserted through the cork of the bottle and hermetically sealed. The oil shall then be heated slowly to a temperature not exceeding 80° F. and remain at that temperature not exceeding fifteen minutes. It shall then be chilled until it stands at 32° F., at which point it must stand for five hours and must be clear, brilliant, and limpid at the expiration of that time.

DISCUSSION.

It was evident that there was need of a clearer definition of the "cold test" and some standard method or methods for its determination. These methods were submitted to the following chemists for their opinion and criticism and for suggestions:

A. H. Schmidt, Schwarzschild & Sulzberger, Chicago, Ill.
David Wesson, Southern Cotton Oil Company, 24 Broad street, New York, N. Y.
A. G. Manns, Armour & Co., Chicago, Ill.
W. E. Tinney, Armour & Co , South Omaha, Nebr.
Garland Jones, Armour & Co., Fort Worth, Tex.
C. F. Hagedorn, Armour & Co., National Stock Yards, Ill.
A. V. H. Mory, Armour Packing Company, Kansas City, Kans.
James Boyce, American Cotton Oil Company, 225 East Nineteenth street, Chicago, Ill.
R. D. Oilar, Wilcox Lard Company, Guttenberg, N. J.
J. E. Weber, Proctor & Gamble, Cincinnati, Ohio.
M. H. Ittner, Colgate & Co., New York, N. Y.
Wilson Low, Cudahy Packing Company, Omaha, Nebr.
W. D. Richardson, Swift & Co., Chicago, Ill.
E. K. Nelson, Nelson Morris & Co., Chicago, Ill.
A. H. Gill, Massachusetts Institute of Technology, Boston, Mass.
A. G. Stillwell, Stillwell Provisioner Laboratory, New York, N. Y.
Stillwell & Gladding, 55 Fulton street, New York, N. Y.
W. W. Sanders, Larkin Soap Company, Buffalo, N. Y.

As a result of the correspondence with these chemists, several points were developed.

(1) A number of entirely different methods are classed under "cold test" and perhaps a number of methods would be needed. The following is quoted from a letter from Thomas S. Gladding:

The determination of the "cold test" is an exceedingly difficult and obscure subject. In the case of oil to be used as a *table* oil, the cloud test is the desirable test. In such an oil the clouding may be due to a small amount of water. Such water should not be expelled by preliminary heating, as the object of this test is to secure an oil that shall remain clear and limpid in cold weather.

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[a] Report N. Y. Produce Exchange, 1902, p. 262.

In the case of lubricating oils, the "cold test," or temperature at which the oil thickens, is the object of examination. In such a case, of course, the water should be expelled before making the test. Our experiments have shown that the question of *time* is the most important factor in making this test. Some oils require to be kept at the congealing temperature for a long period, possibly *several hours* before they thicken. In the case of neat's-foot oil, for example, we found a difference of 20° to 30° according to the time used in making the test. We notice that none of the tests given make any special point of time element. We are inclined to believe that the test used by Armour & Co. is the best of any of the methods given, and if improved by the addition of the time element will prove most satisfactory. We suggest the following method:

Determine the "cold test" or cloud test by the Armour & Co. method. Place the bottle containing the sample in a larger, heavier bottle provided with a large cork, so that the inner bottle may be surrounded by an *air space,* then place the large bottle in a bath of cold water of a temperature of 5° *higher* than the preliminary "cold test" already determined. The oil should be constantly stirred by some automatic clockwork or other arrangement. The fall in temperature should not be faster than 1° in fifteen minutes as it approaches the preliminary "cold test" point. When the oil reaches the temperature of the surrounding water and still remains clear at the end of fifteen minutes, the water bath should be slightly lowered in temperature by the addition of ice, or salt and ice, if below 32° F., and the oil should gradually descend 1° every fifteen minutes. The point where it begins to thicken, as shown by the slow movement of the stirrer, should be considered the "cold test" of the sample.

The constant stirring of the sample and a *very gradual lowering* of temperature, not more than 1° every fifteen minutes, are the two points essential to a successful determination of a true "cold test."

Our belief is that if an oil is maintained for a sufficient length of time, say several hours, at the point where it *begins* to thicken it will eventually turn practically solid without further chilling. We should therefore define "cold test" as the congealing or solidifying point of an oil. We also are inclined to believe that the clouding point would also prove to be the congealing point if the oil be kept for a sufficient length of time at that temperature. If experiments should show that this opinion is correct, the definition of "cold test" would be simply the congealing or solidifying point of an oil when such an oil is kept for a *sufficient* length of time at such congealing temperature.

Only experiments with some such test as we propose can answer this question. When the object of the experimenter is not to determine the actual congealing point, but to determine the fact that it is *below* a certain temperature, then the "cold test" as given by the New York Produce Exchange is decidedly the best.

(2) At least two different objects are in view in making the "cold test." First, to decide the temperature at which an oil will become turbid, and, second, the temperature at which an oil congeals or will not flow, the former relating to salad oils more particularly, and the latter to lubricating oils. The first of these tests would more properly be called the "cloud test," as suggested by Dr. Manns, and the second, which refers to the congealing of the oil, the "cold test."

This test was also discussed at the meeting of chemists in Chicago and it was decided that the cooperation of the railroad and navy-yard chemists was needed before the proper work could be done. This was necessary in order to get the standpoint of the consumer as well as the producer. The great need of standard methods for such determinations is recognized by the trade chemists and all are anxious to cooperate in bringing about better conditions.

Standard or official methods are also needed for the determination of moisture and impurities in fats; for making total fatty acid determinations in soap stocks; and for determining the melting point of fats. These should be taken up by the association as soon as possible.

Belfield Test.

A study of the Belfield test was begun two years ago. A method was outlined and six mixtures of lard and beef were prepared by the referee and sent to those who desired to cooperate. The results were unsatisfactory and it was decided to continue the work this year. The same plan was followed of sending out unknown mixtures of lard and beef, and the following letter accompanied the samples:

> I am sending you, under separate cover, six samples of lard and beef mixtures. Will you please examine the same by the Belfield method and give your opinion as to whether beef fat is present. Use the method you consider the most satisfactory, and in making the report give in detail the method employed, especially as to conditions of temperature and other points you consider of importance.

Fourteen sets of samples were sent out and nine of the men reported.

The samples were prepared as follows: Leaf lard was procured and rendered on the steam bath, filtered, and used as a basis for all the samples. Nos. 1 and 3 were the same, being the pure lard. Nos. 2 and 4 consisted of this lard, to which 5 per cent hard tallow was added. The tallow was also rendered in the laboratory. No. 5 contained 10 per cent of the tallow and No. 6, 10 per cent of lard stearin.

Report of A. G. Manns: I consider No. 1, No. 3, and No. 6 pure lards. No. 2, I consider doubtful, but No. 4 and No. 5, I consider as containing beef fat.

Report of A. G. Stillwell: I find that samples Nos. 3 and 6 are undoubtedly pure lard, as in both cases the crystals were very large and of typical form; in samples 1, 2, and 4 the crystals are fan shaped, but appeared to have the beveled edge of lard crystals; the No. 5 was very typical of beef.

I have made samples containing 5, 10, and 20 per cent of beef and find that the 5 per cent one gives crystals closely resembling the Nos. 2, 4, and 1, and therefore should say they contained some beef.

Method employed was to dissolve 5 cc of melted lard in a mixture of 10 per cent absolute alcohol and 5 cc of ether, and after crystallization pour off the bulk of the liquid, leaving the crystals and some soluble fat behind; then dissolve in 20 cc of ether and allow to crystallize.

Report of W. D. Richardson: In my opinion samples 1, 3, and 6 are pure lard and samples 4, 2, and 5 contain beef fat in increasing proportion by the Belfield test; that is, No. 4 contains the least and No. 5 the most.

In making the test I used U. S. P. ether and allowed the crystals to form at as high a temperature as I could obtain sharply defined crystals, in no case going below 12° C.

In case I use anhydrous ether I add 5 per cent absolute alcohol, as the alcohol tends to produce a quicker crystallization, and, in my experience, gives better results than absolute ether.

Report of Julius Hortvet:

Sample 1 shows only lard. No indications of tallow.

Sample 2, decided indications of tallow. Tallow crystals and clusters well formed and characteristic. Some indications of lard, but no well-defined lard crystals.

Sample 3 shows only lard.

Sample 4 shows mostly lard. Some indications of tallow, and some tallow groups quite characteristic.

Sample 5 shows no lard. Sample is chiefly or entirely tallow.

Sample 6 shows lard. A few groups of crystals show slight signs of tallow, but indications are not positive.

Report of R. E. Doolittle:

Sample 1. No crystals of beef stearin obtained.
Sample 2. Beef stearin present.
Sample 3. No crystals of beef stearin obtained.
Sample 4. Beef stearin present.
Sample 5. Beef stearin present.
Sample 6. No crystals of beef stearin obtained.

My method of examination is as follows: Place about 2 grams of the sample in ordinary size (6-inch) test tube, and melt the sample at a low temperature in water bath, about 50° to 60° C. Allow to cool slightly and dissolve in 12 to 15 cc of ordinary ether, shaking up well with slight warming to get a uniform mixture. Stopper tube with cotton and allow to cool to room temperature, and then place in ice chest and keep at as near 20° C. as possible for 24 hours. If layer of crystals has formed at the end of this time they may be removed by small glass tube and examined. If none or but a small amount of crystals has formed, allow to stand longer, 36 to 48 hours, before making examination. Care should be taken, however, that the ether does not evaporate too low before crystals form, as crystals obtained from the concentrated fat-ether solution do not have the distinctive characteristic shape of lard. The volume of ether should not diminish more than one-half. Some of the crystals are then placed on a slide, with a small drop of olive oil, if needed, a cover glass pressed down over them and examined with compound microscope, using first a low power, and if need be a higher power, to obtain the shape of the ends of the crystals. The important characteristic in the identification of lard crystals is the angular chiseled shaped ends, while those of beef stearin are more round and have pointed ends. Often considerable assistance is given by recrystallizing in the following manner: Decant the ether, melt the crystals, dissolve in ether and crystallize as before, taking the same precautions regarding temperature and volume of ether. Samples containing beef show on recrystallization the beef stearin crystals in very characteristic form. Some samples of lard, however, on recrystallizing as above give very long crystals with slightly more pointed ends.

Report of J. A. Hummel:

Sample 1. Lard; no beef fat present.
Sample 2. Lard and tallow.
Sample 3. Lard; no tallow.
Sample 4. Lard and tallow.
Sample 5. Tallow; no lard seems to be present.
Sample 6. Lard; no tallow.

The following method was used: The samples were melted at a low temperature and about 3 grams placed in a test tube, and when cool 25 cc Squibbs' ether added and shaken. The test tube was plugged with cotton and allowed to stand at a temperature of about 20° C. The temperature varied about 2° either way. Twenty-four hours was sufficient to crystallize all of the samples, though No. 3 was very slow.

Report of A. Lowenstein: In carrying out the tests the following method was pursued:

Three grams of the sample were dissolved in 20 cc of ether in a test tube 5 by $\frac{7}{8}$ inches. The tube was then loosely stoppered with cotton and placed in a room at a temperature of 55° F. It is allowed to remain at this temperature for fifteen to twenty hours, after which time a sufficient quantity of crystals have been formed. The crystals adhering to upper walls of the tube (formed by surface evaporation) are then removed with a clean cloth and the ethereal solution decanted through a filter paper. The crystals at the bottom of the tube are transferred to the filter with a small quantity of ether (cooled to the temperature at which the crystallization was conducted). The filter is allowed to drain thoroughly, and then the crystals are gently pressed between filter papers. The crystals are then mounted in cotton-seed oil and examined with a magnification of 110 to 220 diameters.

It has frequently been stated that the temperature at which the crystallization is conducted is an important feature of this method. I made some tests at 50° F., 55°, 60°, 65°, and 70° F., but did not find any very great difference in the structure of the crystals thus obtained when viewed under the microscope. At 50° F. and 55° F. a layer of crystals about one-eighth inch thick were obtained in sixteen to eighteen hours. At 60° F., about the same quantity in twenty hours, and at 65° F. and 70° F. in about forty hours.

The following are our results on the samples submitted: Samples Nos. 2, 4, and 5 contain beef fat. Samples Nos. 1, 3, and 6 contain no beef fat.

Report of Mr. Bloor:

No. 3. Lard only.
Nos. 2 and 6. Lard, with small admixture of beef fat.
No. 1. Lard, with larger admixture of beef fat.
Nos. 4 and 5. Lard, with large admixture of beef fat.

Method used: Two to 5 grams of fat were dissolved in 20 cc of a mixture of equal parts of absolute alcohol and ether in test tubes. The samples were allowed to stand overnight at about 20° C., the tubes being loosely stoppered with cotton. The crystals were then filtered off, washed three times with small amounts of ether, and then recrystallized as follows: The crystals were dissolved in a test tube in about 5 to 10 cc of warm ether. Double this amount of alcohol was then added and the whole set away for five hours at 15° C. The crystals then formed were examined with powers of from 55 to 480 diameters magnification, using alcohol-ether mixture as a mountant.

Even with check samples of pure lard, pure tallow, and known mixtures of these, examined under the same conditions, I do not feel confident of the results obtained.

Report of A. B. Adams: Samples Nos. 1, lard and beef; 2, lard; 3, lard and beef; 4, lard and beef; 5, lard; and 6, lard.

Nos. 2, 4, and 5 probably contain lard stearin in addition to the lard.

The method followed was as follows: Take 3 to 4 grams of the fat and dissolve in 20 cc of ether in a large test tube, which is loosely plugged with cotton and allowed to stand eighteen to twenty-four hours at 20° C. Pour off the ethereal solution from the crystals which have separated, mount same with cotton-seed oil, and examine under the microscope. Use a magnification of 95 and 230.

These reports indicate that where a satisfactory method is used there is no difficulty in detecting small additions of beef to lard. The most important point, however, is that the addition of 10 per cent of lard stearin to No. 6 did not interfere with the method, as has been claimed by some. A number of important points are brought out in the methods used by the various men, and by adopting some of these a satisfactory method may be devised, but further work is needed.

RECOMMENDATIONS.

(1) Study of methods for determination of moisture and impurities in fats.

(2) Method for making total fatty acid determinations in soap stock.

(3) Study of method for "cold test."

(4) Further study of drying of fatty acids in the titer test.

(5) Further study of the Belfield test.

(6) That the Hanus method as given in the proceedings of 1903[a] be adopted as official for the determination of iodin absorption of oils and fats.

(7) That the method for the titer test, given on page 64, be adopted as provisional.

REPORT ON SPICES.

By A. L. WINTON, *Associate Referee.*

The work of the year has been confined to the analyses of prepared mustard, with the view of developing suitable analytical methods, and gaining an idea of the range in composition of the commercial product.

DEFINITION.

No definition for prepared mustard has yet been adopted by the association, but it seems reasonable that the product should consist entirely of ground mustard seed (or mustard flour, *i. e.*, the ground decorticated seed), spices, salt, and vinegar. Cereal products and other starchy make weights, mustard hulls, and chemical preservatives, are obvious adulterants. Tumeric is not only a color, but also a spice, and its use is therefore unquestionably permissible. Coal-tar colors, at least when they conceal inferiority, would, according to the laws of some States, be classed as adulterants.

ANALYSES OF PREPARED MUSTARD.

Preliminary work on the analysis of this product was carried out in 1904 by the writer, with the assistance of Mr. M. Silverman. Certain analytical difficulties were, however, encountered, which rendered the work incomplete. During the present year these difficulties have been overcome, and quite complete analyses have been made of 28 brands found on sale in Connecticut. These analyses were made by Mr. I. A. Andrew. The maxima, minima, and average results of the analyses of the samples found to be free from cereal starch are given in Table I, and of those containing cereal starch in Table II. In Table II are also given for comparison the maxima, minima, and average results of six analyses of whole mustard seed reported by Leach.

Calculated to the dry fat-free and salt-free material, the samples free from cereal starch contained somewhat more ash, crude fiber, and reducing matters by direct inversion than mustard seed, but this is partly explained by the presence of spices with high percentages of these constituents. Added sugar may have been present in small amount in some of the samples. In one case at least the high per cent of fiber (14.12 per cent), and reducing matters by direct inversion (24.34 per cent), and the low per cent of protein (32.01 per cent), may be attributed to added mustard hulls. Excluding these results, the maxima for crude fiber and reducing matters by direct inversion are, respectively, 12.32 per cent and 23.13 per cent, and the minimum for protein is 36.13 per cent.

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[a] U. S. Dept. of Agr., Bureau of Chemistry, Bul. 81, pp. 63–64.

From these analyses it appears that a mixture of ground mustard seed, spices, salt, and vinegar should not contain more than 12 per cent of crude fiber, more than 24 per cent of reducing matters by direct inversion, nor less than 35 per cent of protein.

In the samples examined, coal-tar dyes (nitro or azo colors) were detected in 14 samples, and salicylic acid in 4. As these do not materially alter the percentage composition, they may, for our purpose, be disregarded. Turmeric was found in 11 samples, but this, as has already been stated, should be classed as a spice.

TABLE I.—*Analyses of prepared mustard containing cereal starch.*

Serial No.	In the material as sold.											In the dry fat-free and salt-free material.				
	Water.	Acidity calculated as acetic acid.	Total solids.	Total ash.	Common salt.	Ash other than salt.	Protein.	Crude fiber.	Crude starch.[a]	Nitrogen-free extract.	Fat.	Ash.	Protein.	Crude fiber.	Crude starch.[a]	Nitrogen-free extract.
	P. c.	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*
12688	80.18	2.65	17.17	2.28	1.60	0.68	3.06	1.04	6.81	9.26	1.53	4.84	21.80	7.41	48.50	65.95
12687	79.85	2.72	17.43	2.45	1.51	.94	4.22	.94	3.71	6.83	2.99	7.27	32.64	7.27	28.69	52.82
12691	85.63	2.78	11.59	2.48	1.66	.82	2.37	1.20	2.18	4.08	1.46	9.68	27.97	14.17	25.73	48.18
12690	84.45	2.72	12.83	2.78	2.08	.70	3.00	1.00	2.97	5.04	1.01	7.19	30.80	10.27	30.49	51.74
12705	83.87	2.60	13.53	2.94	2.21	.73	3.00	1.59	2.24	3.82	2.18	7.99	32.82	17.40	24.51	41.79
12701	87.32	2.79	9.89	2.45	1.97	.48	1.53	1.32	2.12	3.83	.76	6.70	21.37	18.44	29.61	53.49
12702	79.14	3.42	17.44	2.80	1.89	.91	3.34	1.03	6.93	8.98	1.29	6.38	23.42	7.22	48.60	62.98
12700	78.69	3.54	17.77	2.37	1.55	.82	4.19	1.20	4.57	7.08	2.93	6.17	31.53	9.03	34.39	53.27
12685	81.43	2.91	15.66	2.82	2.08	.74	3.50	1.04	2.98	5.05	3.25	7.16	33.89	10.08	28.85	48.87
12704	81.14	2.86	16.00	4.21	3.39	.82	3.37	1.26	3.45	5.56	1.60	7.45	30.61	11.44	31.34	50.50
12692	84.70	2.80	12.50	2.83	2.20	.63	2.94	.96	3.13	4.80	.97	6.75	31.51	10.29	33.55	51.45
12694	70.44	1.86	27.70	3.03	1.87	1.16	6.38	.22	13.69	15.35	2.72	5.02	27.61	.95	59.22	66.42
12696	79.57	2.39	18.04	3.34	2.60	.74	4.31	1.16	5.39	8.05	1.18	5.19	30.22	8.13	37.80	56.46
Maximum	85.63	3.54	27.70	4.21	3.39	1.16	6.38	1.59	13.69	15.35	3.25	9.68	33.89	18.44	59.22	66.42
Minimum	70.44	1.86	9.89	2.28	1.51	.48	1.53	.22	2.12	3.82	.76	4.84	21.37	.95	24.51	41.79

[a] Reducing matters by direct inversion calculated as starch.

TABLE II.—*Analyses of prepared mustard free from cereal starch.*

Serial No.	In the material as sold.											In the dry fat-free and salt-free material.				
	Water.	Acidity calculated as acetic acid.	Total solids.	Total ash.	Common salt.	Ash other than salt.	Protein.	Crude fiber.	Crude starch.[a]	Nitrogen-free extract.	Fat.	Ash.	Protein.	Crude fiber.	Crude starch.[a]	Nitrogen-free extract.
	P. c.	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*
12689	76.49	3.66	19.85	3.15	1.95	1.20	4.53	0.92	2.35	5.07	6.18	10.24	38.65	7.85	20.05	43.26
12695	79.26	3.22	17.52	3.45	2.53	.92	4.44	1.09	2.16	4.24	4.30	8.61	41.53	10.20	20.20	39.66
12698	79.72	2.98	17.30	3.10	2.13	.97	4.22	1.39	2.70	5.09	3.50	8.31	36.16	11.91	23.13	43.62
12945	79.00	3.03	17.97	3.16	2.06	1.10	4.40	1.48	2.02	5.03	3.90	9.16	36.64	12.32	16.82	41.88
12699	79.45	2.80	17.75	4.79	3.69	1.10	3.81	1.68	2.90	5.31	2.16	9.24	32.01	14.12	24.37	44.63
12686	73.01	3.32	23.67	3.09	2.03	1.06	6.12	1.12	2.92	6.11	7.23	7.35	42.47	7.77	20.26	42.41
12683	74.61	3.17	22.22	3.12	1.87	1.25	5.09	1.14	2.60	6.06	6.81	9.23	37.59	8.42	19.20	44.76
12681	83.68	3.00	13.32	2.60	1.78	.82	3.62	.77	1.83	4.21	2.12	8.70	38.43	8.17	19.43	44.70
12682	81.36	2.91	15.73	3.32	2.28	1.04	4.16	1.04	2.37	4.76	2.45	9.45	37.82	9.45	21.55	43.28
12680	77.30	2.80	19.90	3.64	2.66	.98	5.50	1.23	2.44	5.05	4.48	7.68	43.11	9.64	19.13	39.57
12684	79.17	3.18	17.65	3.06	2.13	.93	4.25	1.14	1.94	5.08	4.12	8.16	37.28	10.00	17.02	44.56
12703	81.66	2.98	15.36	2.80	1.80	1.00	4.56	1.06	2.42	4.47	2.47	9.02	41.12	9.56	21.82	40.30
12693	77.41	2.74	19.85	4.03	2.90	1.13	5.35	1.15	2.48	4.72	4.60	9.15	43.32	9.31	20.08	38.22
12697	77.78	2.90	19.32	3.73	2.58	1.15	5.19	1.16	2.49	5.05	4.19	9.16	41.35	9.24	19.84	40.25
12951	78.90	3.10	18.00	3.79	2.48	1.31	5.40	1.28	2.31	4.30	3.23	10.66	43.94	10.42	18.80	34.98
Maximum	83.68	3.66	23.67	4.79	3.69	1.31	6.12	1.68	2.92	6.11	7.23	10.66	43.94	14.12	24.37	44.76
Minimum	73.01	2.74	13.32	2.60	1.78	.82	3.62	.77	1.83	4.21	2.12	7.35	32.01	7.77	16.82	34.98
Average	78.59	3.05	18.36	3.38	2.32	1.06	4.71	1.17	2.40	4.98	4.12	8.94	39.44	9.89	20.11	41.73

[a] Reducing matters by direct inversion calculated as starch.

TABLE II.—*Analyses of prepared mustard free from cereal starch*—Continued.

SIX SAMPLES OF WHOLE MUSTARD (LEACH).

	In the dry fat-free and salt-free material.				
	Ash.	Protein.	Crude fiber.	Crude starch.[a]	Nitrogen-free extract.
	P. c.	*P. c.*	*P. c.*	*P. c.*	*P. c.*
Maximum	7.64	48.31	10.33	15.91	48.55
Minimum	6.28	37.50	7.24	11.94	37.84
Average	6.83	44.31	8.05	13.82	40.81

[a] Reducing matters by direct inversion calculated as starch.

METHODS.

Descriptions of the following methods, which in our experience had been found satisfactory, were submitted early in the year to such analysts as expressed interest in the subject. Although none of these has reported any results, a number have commented favorably on the methods, and none have criticised them adversely.

Analysis of prepared mustard.

Sampling.—The solid portion of the material is commonly in a finely divided condition and does not require grinding, but as it tends to settle, leaving a more or less clear liquid on the surface, thorough mixing is absolutely essential. This may be accomplished by stirring with a spoon immediately before removing each portion for analysis.

Solids.—Dry 5 grams in a flat-bottomed platinum dish on a water bath until the mixture appears dry, and finally dry to constant weight at 100° C. in a water oven.

Ash.—Burn the dry residue obtained in the determination of water to a white ash in a muffle furnace at a heat below redness.

Salt.—Determine chlorin in the ash with silver nitrate, either gravimetrically or volumetrically, using potassium chromate as an indicator.

Ether extract.—In a capsule place 10 grams of the material, about 30 grams of sand, and a short stirring rod. Heat on a water bath, with constant stirring, to apparent dryness and finish the drying in a water oven. Grind until all the lumps are broken up, and extract for 16 hours in any suitable apparatus with absolute ether. Dry the extract at 100° C. and weigh.

Protein.—Determine nitrogen by the Kjeldahl method and multiply the results by 6.25.

Crude fiber.—Weigh 8 grams of the material (equivalent to about 2 grams of dry matter) directly into an Erlenmeyer flask and proceed as with spices,[a] except that care is taken to add at first only a small amount of 1.25 per cent acid or alkali, and shake thoroughly until all lumps are broken up. If this precaution is not taken, the lumps will resist the action of the acid or alkali and the results will be high. Extraction of the fat previous to the treatment is impracticable, as this necessitates preliminary drying, after which the material forms a horny mass.

This method is valuable as furnishing indications as to whether the product is made from ground mustard seed, mustard flour (decorticated ground mustard seed), or mustard hulls, comparisons being made of the results calculated to a water-free, fat-free, and salt-free basis.

Reducing matters by direct inversion calculated as starch.—Proceed as with spices [b] except that 10 grams of the material are treated directly with 200 cc. of water and 20 cc. of 25 per cent hydrochloric acid without previous washing or extraction, and the solution is made up to 250 cc before filtering and drawing off the aliquot.

This method is of value in detecting starchy adulterants, although the results obtained are higher than the true percentage of starch, owing to the conversion of constituents of the mustard seed into copper reducing substances and the frequent presence of water-soluble carbohydrates. As the starchy matter used is often in the form of paste, preliminary washing with water is impracticable.

Acidity.—Weigh out 10 grams into a 200 cc graduated flask, make up to the mark with water, shake, filter through a dry paper, and determine the acidity in 100 cc by titration with N/10 potassium hydrate solution, using phenolphthalein as an indicator.

Tests for dyes.—Test for turmeric by the boric-acid method or by microscopic examination.[c] Examine for coal-tar colors by Arata's or Sostegni and Carpentieri's method [d] with subsequent examination of the dyed wool, Turmeric also imparts a dull yellow color to the wool, but this color is changed to brown-red with alkali and does not give marked color reactions with concentrated hydrochloric or sulphuric acids. Nitrocolors dye the wool brilliant shades of yellow, which on treatment with hydrochloric acid are partially bleached (salts of dinitrocresol) or remain unchanged (tartrazin, etc.). The azo colors commonly used are changed to crimson or violet on addition of strong acid to the dyed fabric or the filtered aqueous solution of the original material.

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 65, p. 58.

[b] Loc. cit., p. 57.

[c] Loc. cit., p. 120.

[d] Loc. cit., p. 112.

Tests for preservatives.—Tests for boric, salicylic, and benzoic acids by the usual methods.[a] As shaking with ether dissolves a large amount of fat, salicylic or benzoic acid should be separated from this fat by sublimation, solution in dilute alcohol, or conversion into the ammonium salt and solution in water. These acids may also be obtained from the original material by distillation.

CACAO STARCH.

By Burton J. Howard.

For years the microscopic test for foreign starches in cacao and chocolate preparations has been considered final and sufficient. It therefore occasioned no small degree of surprise when about a year ago the announcement was made that it was possible that cacao starch might be changed during heating in the process of roasting into aggregates resembling corn, wheat, barley, rye, or even potato starch so closely as to make the microscope of little or no value in proving the presence of these starches in cacao preparations. As was to be expected, the announcement was heralded widely by the daily press, for its bearing on food-inspection work was apparent. In fact, the whole matter sprang out of a case being prosecuted in connection with the food laws of one of the States. The only notice which the writer has seen upon the subject in any of the scientific journals is an abstract[b] of a paper given by Prof. Henry Kraemer before the Society of Plant Morphology and Physiology at Philadelphia last winter. In view of the importance of the question in the analysis of cacao preparations by the Bureau of Chemistry in connection with its imported food work, it was decided to look somewhat further into the matter.

The notice above cited is altogether too meager to be used as a basis for criticism, as it simply states that "the author called attention to the alteration in the compound starch grains of the seeds of *Theobroma cacao* on the application of heat, producing masses resembling the natural starch grains of corn, wheat, barley, rye, and potato in size and shape and showing in some cases even a concentric or excentric lamellated structure." As inferred in the above, it was considered to have been accomplished by the agglutination of the compound starch grains of the cacao bean. The analysts most directly concerned in the legal case mentioned above informed us that the tests were made by heating sections of the cacao bean upon a microscopic slide, but that only very rarely were such aggregations produced. The resulting masses were not tested with the micropolariscope.

In preparing for our study of the subject, 14 samples of raw cacao beans obtained from two prominent American chocolate manufacturers as well as several samples in our own collection were used. The samples obtained from the manufacturers included the following varieties: African, Trinidad, Caracas, Java, Bahia, Caraquez, Surinam, Grenada, Para, and Ecuador. Cacao starch occurs in the loose parenchyma cells of the bean together with the fat and other cellular contents. These parenchyma cells vary in size from 15 to 30 microns in diameter, and in rare cases cells 50 microns long by 15 wide were found, but such cells occur somewhat removed from the fibro-vascular vessels and contain only a small amount of starch. They usually, however, approach isometric dimensions, though in some cases the length may be three times the width. The starch grains occur in these cells in numbers of from 1 or 2 up to 18 or 20, and in these extreme cases may occupy about one-half the cell capacity. The writer has not yet found that number to be exceeded. It should be noted that the cells which contained starch in greatest abundance always appeared to be in close proximity to fibro-vascular bundles, and, further, that such cells were smaller than those removed from the bundles. In no case was a large amount of starch found in cells of more than about 30 microns diameter.

Cacao starch occurs as single grains or as simple representatives of compound grains. The single grains are nearly spherical in form and usually show a fairly strong, almost central hilum. The common type of compound grains is that in which 2 or 3 grains are attached. This number, however, is not infrequently increased to 4 and occasionally to 5, which seems to be the maximum. When these aggregates are broken up, grains with the sugar-loaf form result, but from the nature of the original, no grains appear which are truly polygonal, as is the case of corn, oats, rice, or buckwheat, these occurring in aggregates of sometimes 40 or more grains, some of which are crowded on all sides by other grains, thus producing the polygonal type.

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 65, pp. 108–110.

[b] Science, *21:* 504.

In size the grains vary somewhat in the several varieties. Ewell[a] gives the maximum size as 12 microns. Tirsch and Osterle[b] give for the Caracas variety 4 microns, for Bahia 6–8, for Port Cabello 9, for St. Thomas 3–5, for Guajaquil 3.3–5, Trinidad 6–11, for Venezuela 8–14, and for Ceylon 5–7, and Kraemer[c] gives the size as being 4–8, and Leach[d] as 2.4–12.7 microns. The writer found the following to be true of the samples examined:

In one specimen of Trinidad bean a starch grain of 17 microns was found, while for the other varieties 14 was found as the limit before roasting, though in a few varieties it was smaller. The same specimens were also examined after roasting, and though in some cases there seemed to be a slight increase in size, yet there was no evidence that the increase ever exceeded 14 per cent, and in most cases it was much less. In other words, the maximum size of grains after roasting was never more than 14 per cent over the maximum size occurring in the raw state. This point should be borne in mind, since it has a direct bearing upon another phase of the question. It was also found that, in each variety examined, the grains of maximum size were the simple grains; that is, it seems to be true that the compound aggregates rarely exceed in size, and then only slightly, any of the simple grains in the same specimen of bean.

With polarized light, cacao starch shows an ill-defined though fairly strong cross, and in this, as in other starches, the bars cross at the hilum. In the compound grains each component grain has its own independent cross which can usually be observed, and, on account of the small number of grains making up the aggregates, the confusion of effect which is so pronounced in the case of rice and oat starch is very slight in the cacao.

In order to determine the effect of heat upon the grains, sections of the bean were cut and scattered along the length of a microscope slide. The slide was then held over a flame so that the heating was most intense at one end and lessened in degree toward the other end. The heating was carried on slowly until a deep browning of the sections in the hottest part of the slide had occurred. After allowing to cool, ether was carefully flowed over the slide to remove the bulk of the fat. The material thus prepared was then examined microscopically. The largest starch masses found after such treatment were of 20 microns diameter. Scores of mounts were made and examined, but in only one mount did there occur a grain which would be confused with corn starch because of its size, form, and activity toward polarized light, and that mount was made immediately following an examination of a sample of corn starch and was probably a contamination, for though starch masses have repeatedly occurred which in size equaled the average corn starch grains and resembled in form the grains found in some of the softer varieties, yet, with this single exception, the comparison failed when the test with polarized light was made.

Thus far, we have absolutely failed to produce starch masses in shape and size which would be mistaken for wheat or potato starch. In this connection our experience with a certain slide is of interest. When the slide was examined there were found present two bodies which in size and shape very strongly resembled wheat or some grains from potato. Even the striations on the surface seemed to be present. An examination with iodin and then with alkanna solution showed them, however, to be oil globules and not starch grains at all, and that after most of the fat was supposed to have been removed by ether. Experiments were also made on sections which had a larger amount of moisture present, but

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 13, pt. 7, p. 948.

[b] Anatomischer Atlas der Pharmacognosie und Nahrungsmittelkunde, p. 23.

[c] Botany and Pharmacognosy, p. 299.

[d] Food Inspection and Analysis, p. 306.

in these tests, as in the others, no large-sized starch masses were formed. When cacao starch is heated with water sufficiently to cause the grains to swell, the segments of the compound grains retain their identity, but their activity toward polarized light is entirely destroyed.

The behavior of corn starch which has been changed by heat into dextrin is of interest in this connection. Such grains, though they may retain their original form and size as well as their polariscopic activity while dry or mounted in alcohol, lose all these characteristics to a greater or less extent when mounted in water, for when dextrin is moistened more or less swelling of the grains takes place. In no case does the writer know of an instance where any variety of starch gives activity toward polarized light in any part of a starch grain in which perceptible swelling has occurred, no matter from what cause such swelling was produced, whether from acid, moist heat, chloral hydrate, Millon's reagent or caustic alkali; furthermore when the polariscopic activity has once been impaired by any of the above means, no way has thus far been discovered by which the activity can be restored. Even in the case of corn dextrin in which the conversion has been incomplete, so that when water is added only the outer layers swell up sufficiently to lose their activity, experiment shows that a subsequent desiccation is insufficient to restore the activity which has been lost.

In view of the above, and when it is remembered that the raw starch masses normally seem never to exceed 18 microns, and that the typical grains of wheat and potato starch are from 27 and upward in size, thus requiring an increase in the size of the grains of one-half in order to produce masses of such size, it seems impossible to conceive of cacao starch being transformed by swelling to resemble in size and form any of the larger kinds and yet retain even their original activity toward polarized light, to say nothing of having that activity changed in its leading characteristics; that is, from a compound to a simple cross and at the same time intensified in degree of activity.

Again, when it is borne in mind that the total number of grains in the individual cells, even the highest number, is comparatively limited, rarely, if ever, exceeding 18 or 20 and forming several groups within the cell wall (all of which if united in one solid mass would not equal in size a very moderate size wheat or potato starch), we are at a loss to see how a sufficient number of grains could chance to come together to form such large aggregates as to resemble in shape and size these larger varieties of starch. This could only be accomplished, as we see it, by the migration of the starch grains *in toto* from one cell to another, and that through the solid cell wall without rupturing the same. Even if such an inconceivable change took place, it is still impossible to conceive, with our present knowledge of starches, that we should find in such aggregations the necessary characteristics of polariscopic activity as are present in the larger types of starches.

Therefore, in conclusion, we believe that with the microscope and the micro-polariscope the presence of foreign starches in cacao products can be established. As has already been indicated, care must be exercised in making sufficient microchemical tests to establish beyond a doubt that the masses under consideration are composed of starch, since fat globules may, under certain circumstances, strongly resemble some of the larger starch grains; furthermore the grains must occur in sufficient numbers to preclude the possibility of their presence having come about by accidental contamination.

The PRESIDENT. It gives me great pleasure to announce one of the best friends the association has ever had—the Secretary of Agriculture, Mr. James Wilson.

ADDRESS BY THE SECRETARY OF AGRICULTURE.

Hon. JAMES WILSON. Mr. President, Ladies and Gentlemen—I come this morning merely to bid you welcome to the Capital City, to express the hope that you will enjoy your visit among us, and to assure you that I not only highly appreciate the work you are doing, but am well satisfied that all the people in the United States and outside of the United States recognize that the American chemist is doing something for righteousness in the world. He wants honest, fair, and square dealing. The money-making people are not always scrupulous concerning how money is made. Good men want to do honest work and give everybody with whom they come in contact a square dealing, and I think a very large majority of our people in the United States are honest people who intend to do what is right, but there is a small per cent of men among us who are not disposed to do what is right if by doing what is wrong they can make money a little faster.

One of the important directions in which the American people are now turning their attention is to pure foods. There has been something done by the influence of the good people of the United States, working through the chemists' association, to create a better understanding as to what a man's rights should be when he goes into the market to buy. Under the authority of Congress we have been inquiring into importations from abroad, and we have had some success in stopping the importation of adulterated and wrongly labeled goods. I think Doctor Wiley has substantially succeeded in excluding a very large proportion of all the goods of that kind brought into the United States, and that it may be truthfully said of the merchants on this side of the water who deal in these products that they really did not know the character of these goods, but since it has been brought to their attention the honest merchants have stopped handling them. And so we are making some progress along these lines, but that does not go far enough. I do not know whether I have told the story to you before, but I tell it occasionally to illustrate the point under discussion. I was in St. Paul, Minn., one day—I was at home in Iowa in those days—and I called on a young man named Mr. Eaton (I think he is here now), who was looking into the purity of goods imported into that State, in behalf of the Minnesota people. I said, "Well, Mr. Eaton, what have you been doing this morning?" He said, "I have been looking into a carload of vinegar." "And you found it all right?" said I. "No," said he; "I found it all wrong." "But," said I, "it will then go back to the dealer." "No," said he; "it will go to Iowa; you haven't any food law there." Now, that illustrates just what happens under existing conditions. So the demand comes from our people generally that the one power in the land that can look into and regulate interstate commerce shall do so, in the interests of the American people, with regard to food products. It is a fair proposition that when a man goes to market to buy goods they shall be what they are represented to be, and this is about all that is asked. It takes some time, however, to get legislation along these lines, as a certain number of people make money by misrepresentation. It took some time to get a law to stop the practice of selling oleomargarin, manufactured for 6 cents a pound, as cow's butter, for from 15 to 25 cents a pound, but the American people would not be still; they insisted upon it. I recall a story that Colonel Henderson told with regard to his own constituents. They said, "Colonel Henderson, we want a law requiring people who sell oleomargarin to sell it as oleomargarin." "Very well," said he, "I will vote for it." "But you can secure the legislation, can't you?" Says he, "I don't know." "Very well, if you don't know, we will send some one who does know." When the American people reach that frame of mind they always get the legislation desired, and they are working up to that point regarding pure foods. They are going to insist, and they always get things their own way. They are just a little slow sometimes, and they always want to get their facts well in hand before taking a stand of this kind, but we are going to get legislation, gentlemen, so that when a man, even though he is not a chemist, goes to market to buy goods they will be properly labeled, properly branded, and they will not be adulterated as they are now in so very many cases. This is uppermost in the minds of the American people, and you, gentlemen, are in a position to give the people the facts along these lines. We all look to you to tell us what the facts are, not only with regard to our imported foods, but with regard to interstate commerce. The American people, as I said before, and I want to say it again, because I want to emphasize it, an exceedingly large majority of the American people want fair play, but we have some who do not, and when our legislators are in session here in Washington these men are found around the lobbies, and there is no way by which they can be kept out of the lobbies that we know of.

If the American people speak loud enough the legislation always comes, and you are doing more to bring this about than all other workers put together.

I thank you very much, gentlemen, for listening patiently to my remarks. You know all these facts better than I do. I hope you will have a pleasant time while here in the city. Everyone is glad to see you come; and so I bid you good morning.

REPORT ON ADULTERATION OF DAIRY PRODUCTS.

By A. E. Leach, *Associate Referee.*

No reliable method strictly chemical has as yet been devised for distinguishing between milk to which water has been fraudulently added and milk high in water as given by the cow. In some localities, as in Massachusetts, it becomes necessary for the analyst to distinguish between these two classes of milk, since the law imposes a much smaller penalty for low-standard milk than for milk with added water, the latter being classed as adulterated and rendering the offender liable to a drastic penalty, as in the case of added color or preservative.

It has hitherto been impossible positively to allege added water in milk unless the sample as analyzed was found to stand lower in total solids, or in solids not fat, than the minimum limit for Holstein milk of known purity. This limitation allowed us to place in the watered class extreme cases only, so that formerly many samples that were actually watered were necessarily passed by as simply below the standard.

The refractometric method, first published in the annual report of the analyst of the State Board of Health in 1903,[a] has since been thoroughly tested in a number of laboratories and its reliability has been established. From our own experience and that of others during the last two years we have had no occasion to change in any way the method as originally worked out, and this method in detail will be found in the recommendation at the close of this report. Briefly, the milk is curdled under certain fixed conditions and the clarified milk serum is examined by means of the Zeiss immersion refractometer. To anyone not familiar with the possibilities of the refractometer, the difference in refraction between the sera of pure and watered milk is surprising, and it is this physical characteristic that will in most cases give a positive clue as to whether or not the milk is pure.

Data on as many samples of milk of known purity as possible have been collected with a view to establishing the minimum refractometric reading for the serum of pure milk. Most of our attention has been paid to milk from Holstein cows, which of all breeds are most inclined to give milk below the standard. In fact, we have sought out as far as possible particular cows which gave low-standard milk, and it has been our good fortune to find a good many such. At first we were inclined to adopt 40 as the minimum refractometric reading at 20° of the serum of pure milk, but from occasional samples that were found to run below this figure we have later been inclined to adopt 39 in the interest of conservatism. In fact, if a milk serum is found with a refraction lower than 39, it is safe to allege that the sample was fraudulently watered, especially, if in addition to this, the solids not fat stand below 7.3 per cent.

From the perishable nature of milk it is not easy to secure collaborative work on the same samples, especially when sent to a great distance. Indeed, such cooperative work is hardly necessary in a method of this sort, wherein there would be no reason to suppose that, with due care, readings made by different chemists would not conform closely to each other.

The immersion refractometer, in spite of its wide field of usefulness to the food chemist, has not as yet come into very general use. The referee has, however, been fortunate in securing the cooperation of two analysts who have used the instrument extensively and have secured most satisfactory results by its application to the examination of milk serum, using the method under consideration.

Mr. R. B. Fitz Randolph, of the State laboratory of hygiene, New Jersey, has sent analytical data on 106 samples of milk analyzed by him, including eight samples of known purity. I have also been fortunate in securing analytical data obtained by a most complete examination of 180 samples of milk of known purity, taken from herds of various breeds in different parts of Great Britain. This work was done by Mr. J. Hanley, F. I. C., F. C. S., chemist of Messrs. J. Bibby & Sons, of Liverpool, England, who have kindly permitted him to furnish this information. Mr. Hanley wishes to acknowledge the services of his assistant, Mr. A. Law, in the analytical work.

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[a] Thirty-fifth Ann. Rept. Mass. State Board of Health, 1903, p. 483; J. Amer. Chem. Soc., 1904, *26:* 1195.

Table I.—*Milk of known purity.*

Classification according to total solids.	Limits.	A. E. Leach, Massachusetts State Board of Health.					R. B. Fitz Randolph, New Jersey State Laboratory of Hygiene.					J. Hanley, J. Bibby & Sons, Liverpool, England.				
		Number of samples.	Total solids.	Fat.	Solids not fat.	Refraction of serum at 20° C.	Number of samples.	Total solids.	Fat.	Solids not fat.	Refraction of serum at 20° C.	Number of samples.	Total solids.	Fat.	Solids not fat.	Refraction of serum at 20° C.
Per cent.			*P. ct.*	*P. ct.*	*P. ct.*			*P. ct.*	*P. ct.*	*P. ct.*			*P. ct.*	*P. ct.*	*P. ct.*	
Above 15.	Highest..	2	15.14	6.60	8.54	43.2	-----	-----	-----	-----	-----	1	15.12	5.90	9.22	42.62
	Lowest..		15.10	6.00	9.10	43.5										
14 to 15...	Highest..	-----	-----	-----	-----	-----	3	14.72	5.85	9.16	43.6	10	14.87	6.14	10.25	43.60
	Lowest..							14.01	5.20	8.87	42.5		14.00	4.26	8.66	41.62
13 to 14...	Highest..	1	13.43	4.35	9.08	43.6	2	13.21	4.25	9.11	43.7	38	13.98	5.20	9.48	44.15
	Lowest..							13.16	4.10	8.91	43.3		13.03	3.68	8.45	40.55
12 to 13...	Highest..	13	12.96	4.50	9.04	44.4	1	12.42	3.80	8.62	42.2	73	12.92	4.54	9.94	43.50
	Lowest..		12.11	3.55	8.16	41.4							12.05	2.84	7.82	40.00
11 to 12...	Highest..	22	11.93	3.60	8.49	44.1	2	11.96	3.60	8.96	42.5	50	11.97	5.36	9.40	43.00
	Lowest..		11.03	2.60	7.43	39.9		11.74	3.00	8.14	40.6		11.10	2.30	7.30	39.13
10 to 11...	Highest..	8	10.88	3.45	7.99	41.8	-----	-----	-----	-----	-----	7	10.98	2.86	8.63	41.60
	Lowest..		10.45	2.55	7.43	39.0							10.23	2.18	7.46	40.60

Table II.—*Milk collected for inspection from dealers.*

Classification.	Limits and average.	A. E. Leach, Massachusetts State Board of Health.					R. B. Fitz Randolph, New Jersey State Laboratory, of Hygiene.				
		Number of samples.	Total solids.	Fat.	Solids not fat.	Refraction of serum at 20°.	Number of samples.	Total solids.	Fat.	Solids not fat.	Refraction of serum at 20°.
			P. ct.	*P. ct.*	*P. ct.*			*P. ct.*	*P. ct.*	*P. ct.*	
Above standard of solids (12 per cent.)	Highest...	34	14.54	5.15	10.06	45.0	48	15.37	6.60	9.20	44.6
	Lowest...		12.00	3.10	7.90	40.0		12.00	3.00	7.61	39.6
	Average ..		13.14	4.02	9.12	42.9		12.97	4.17	8.80	42.5
Below standard of solids (12 per cent) but not watered.	Highest...	31	11.65	3.55	9.20	43.9	33	11.97	4.00	9.90	43.3
	Lowest...		10.27	1.50	7.77	39.0		9.12	.35	7.35	39.0
	Average ..		11.04	2.85	8.19	40.7		.....	.....	.....	.....
Milk with added water........	Highest...	58	11.35	4.00	7.77	38.8	17	12.80	6.30	7.27	38.7
	Lowest...		4.69	.25	4.44	28.7		9.64	2.60	6.30	35.8

The accompanying tables show in summarized form the results of the analyses of a large number of milk samples from three widely separated localities. Milk of known purity in all the above cases is understood to have been authenticated as having been milked in the presence of an agent representing directly the laboratory in which the milk is examined and personally delivered by the agent to the laboratory. It is true that abnormalities may occur, whereby in rare instances milk as taken from the cow may show a refractometric reading below 39, but this fact should not interfere with the success of the method. We are especially on the outlook for abnormalities of this kind, and it might be said that out of 233 samples of milk of known purity from Massachusetts, New Jersey, and Great Britain only one authentic instance has come to light, namely, that of a most unusual cow in England, about which Mr. Hanley writes: "A typical heavy milking animal that when in full flow yields 60 pounds of milk per day, is 10 years old, has never had any disease, but has dropped her full quota of eight calves." The results of the analysis of milk from this particular cow have not been included in the table, but for one day were as follows:

Table III.—*Results of morning and evening milking.*

Time of milking.	Total solids.	Fat.	Solids not fat.	Refractometer reading at 20° C.
	Per cent.	*Per cent.*	*Per cent.*	
Morning	10.10	2.64	7.46	38.40
Evening	9.80	2.60	7.20	37.70

A particular study of this cow was afterwards made by Mr. Hanley, who obtained milk morning and evening for 12 days from this same cow, and found the analytical data to vary between the following limits:

Table IV.—*Maximum and minimum results on milkings for 12 days.*

Limits.	Total solids.	Fat.	Solids not fat.	Refractometer reading at 20° C.
	Per cent.	*Per cent.*	*Per cent.*	
Highest	10.53	3.48	7.61	38.55
Lowest	9.27	2.56	6.58	36.20

The method is largely useful in cases where the total solids and solids not fat are not in themselves low enough to indicate the fact that water has been added. Indeed, in one instance recorded by Fitz Randolph added water was indicated positively in a sample of milk standing as high as 12.80 per cent in total solids and 6.3 per cent fat, the immersion refractometer reading at 20° C. being 36.3. This had been watered down from a sample of particularly rich milk, originally standing apparently between 17 and 18 per cent in total solids.

As a further test of the reliability of the method it should be said that a large number of court cases have been successfully brought in Massachusetts for watered milk, basing the complaint for added water on this method. In some cases the milk stood well above 11 per cent in total solids, and without the present method it would be impossible to allege added water. In some of these cases the defendant pleaded guilty without trial. In one case, where the milk stood as high as 11.33 per cent in total solids, the defendant admitted that his milk was watered. I understand further that Mr. Hanley has had occasion to use the method in legal cases in Great Britain with good results.

Comments of R. B. Fitz Randolph.

Immersion refractometer reading.—Fifty cc of the milk are placed in a 100 cc Erlenmeyer flask, 1 cc of 25 per cent acetic acid added, the flasks tightly closed with rubber stoppers, one of which bears a thermometer, the bulb of which dips into the milk. These flasks are placed in a large water bath with flat bottom and surrounded with water above the level of the milk, the flasks being weighted with lead rings to keep them from floating. The bath is placed on a hot plate and heated until a temperature of 70° C. is reached in the flasks, which requires about 25 minutes. The bath is then removed from the plate and allowed to stand with the flasks in it for 15 minutes longer. The flasks are frequently shaken during the heating. The water is then removed from the bath and replaced by shaved ice and water, in which the flasks are allowed to remain until the temperature of the milk is at or below 10° C. The whey is then filtered through S. & S. folded filters No. 588, 12.5 cm in diameter into the beakers, in which the refractometric reading is made. The filtrate is usually slightly turbid, but not sufficiently so to interfere with accuracy in making the readings. The beakers are placed in the refractometer bath, covered with watch-glasses and allowed to remain for 15 minutes before the readings are taken. The temperature of the bath is kept between 18° C. and 22° C. and the readings corrected for temperature by means of the table given in Wagner. The temperature of each beaker is taken with a quick-acting thermometer inside the beaker immediately after the refractometer prism is removed. I have been unable to keep the bath near enough to 20° to do away with the necessity for temperature corrections and believe that if the temperature is kept within a degree or two of 20° C. the corrected reading is accurate enough for all practical purposes. The thermometer which came with my instrument when compared with a standard tested at the Reichsanstalt proved to read 0.2° C. too high. My temperature corrections therefore include a correction for the error of the thermometer.

Comments of J. Hanley.

For the purpose of investigating the reliability of the refractometer as a means of detecting added water in milk, I have examined every sample of certain purity which arrived at this laboratory since July last.

The investigation, which we are still pursuing, aims at determining:

(1) Whether the refractometer can be relied upon to detect water added to milk.

(2) Whether the refractometer indicates the presence of water in milk when the milk is pure.

(3) Making a comparison on the above two points the reliability of the refractometer and the present method of judging by the proportion of nonfatty solids in a milk.

Relying on our scheme of free analysis to our customers, and our 300 British agents, it is easy to procure milk of certain purity from any part of Great Britain.

There is a strong grievance in this country among farmers and dairymen on the question of added water in milk. It is not that the analyst fails to find the water, but that he finds it when it is not there, and it is here the refractometric method shows vast superiority over analytical methods.

In the present report we have 176 samples, all of certain purity. Out of these the analytical method raises a presumption of added water in 47 instances, whereas the physical method has only been mistaken in two cases. The physical method is, therefore, 24 times more accurate than the chemical, and is very seldom misleading.

For the refractometric examination, ten 150 cc beakers with numbers engraved on them from 1 to 10, were placed in consecutive order on the bench, the ten numbered samples following after them all in one line. A graduated glass measure was then filled to the 100 cc mark with the first sample of milk and poured into the first beaker; the same measure was used without cleaning for the second sample, and so on. When the ten beakers were filled with milk, the acetic acid was dropped in from a burette, stirring briskly the while with a glass rod, the stirring continued for about one minute, a watch glass placed on top, and the whole immersed in a water bath, which at the outset registered 71° C.

This water bath holds ten beakers, and is provided with a thermostatic regulator. As soon as the first beaker is placed therein, the temperature falls to 70° C., and subsequently never falls below 69.5°. The time at which the beaker was to be removed from the water bath was marked with a glass pencil on the cover; then another beaker was acidified and stirred as before, each one occupying two minutes.

Two minutes after the tenth beaker was placed in the water bath, it was time to place the first one on ice, and when the sixth beaker was placed in the ice, it was time to filter the first one. Every two minutes after that one beaker was removed from the water bath, placed in the ice bath, and another taken out of the ice bath and filtered.

When 27 cc had filtered through, the time was noted, the small beaker was covered with a watch glass, and transferred to a wooden tray. When the ten filtrates were ready, all were placed in the cooling trough of the refractometer. At the same time that the small beakers were immersed in the refractometer trough, the instrument itself was immersed in the central opening, and after the lapse of one hour the readings were taken. The refractometer was removed from the trough, wiped with a dry towel, the small beakers removed from the trough, wiped on a towel to get rid of the air bubbles and replaced in the trough, the refractometer immersed in the beaker, and the reading taken at once. The refractometer was then removed, wiped with a towel, and placed in the next beaker, after removal of the air bubbles from the bottom of the latter.

To obtain sharp readings we find it is important to remove the air bubbles from the bottom of the beaker, to keep the ground glass on the bottom of the trough clean, and the mirror free from dust.

What has struck me as the most interesting point so far is that apparently the refractive power is not to be led out of the path of virtue by richness, but betrays added water in rich milk as easily as in poor milk. This will be an extremely valuable point if further experience confirms it. You will note that we have met only one cow yielding a reading below 39.

Concordance of duplicate results.—My invariable rule in testing a new method is to determine, in the first instance, whether the method yields concordant results. With this object in view, I obtained a sample of milk from a shop and tested 6 portions separately. The results are highly satisfactory, all reading exactly 41. Since the above experiments I have had several other samples of the strictly concordant results the method yields.

Watered samples.—The same milk was watered with proportions of water varying between 10 and 25 per cent. The results are as follows:

	Refractometer at 20° C.
Original milk (purity unknown)	41.00
Same milk with 10 per cent of water added	38.10
Same milk with 15 per cent of water added	37.00
Same milk with 20 per cent of water added	35.00
Same milk with 25 per cent of water added	34.30

A survey of the table leads to the belief that for most purposes 40 should be taken as the lower limit, and milk between 39 and 40 should be regarded as very suspicious, presumably watered or abnormal. I am aware that formerly you adopted 40 as the lower limit and no doubt you have seen good reasons to reduce to 39.

I have met a case in which a dairyman was giving the first part of the milk to calves, and selling the last part from each teat. The selling milk, of course, came out very high in fat and low in nonfatty solids, raising the presumption of some 10 per cent added water. This was a case in which we were confidential with the farmer, and he became very wroth that his good, generous intentions should be so grossly misinterpreted. One experienced in analysis of milk would have inclined to the opinion that the nonfatty solids had been displaced by cream. However, it is very satisfactory to find that the refractometer makes no mistake on this point. The serum of the first part of the milk from the udder is identical with the "strippings."

Recommendation.

It is recommended that the following be adopted as a provisional method:

DETECTION OF ADDED WATER.[a]

To 100 cc of milk at a temperature of about 20° add 2 cc of 25 per cent acetic acid (sp. gr. 1.0350) in a beaker, and heat the beaker, covered with a watch glass, in a water bath for twenty minutes at a temperature of 70° C. Then place the beaker in ice water for ten minutes and separate the curd from the serum by filtration through a 12.5 cm plaited filter.

Transfer about 35 cc of the serum to one of the beakers that accompanies the control-temperature bath used in connection with the Zeiss immersion refractometer, the bath being of the type with openings in the top for 10 beakers. Place the beaker in one of the openings, use the ground glass strip at the bottom of the bath, and by means of the regular refractometer heater or similar device maintain a constant temperature of exactly 20° C. in the water surrounding the beaker, using a delicate thermometer, reading to tenths of a degree. Immerse the end of the refractometer in the serum in the beaker, and when the temperature is exactly 20° take the reading on the scale.

If the temperature varies from 20°, the reading may be calculated on that basis by means of a correction table. A reading below 39 indicates added water; between 39 and 40 the sample is suspicious.

Mr. Cochran, in commenting on the use of the refractometer, spoke in part as follows: We have as yet a very limited knowledge of the refractometer and it would seem that even on evidence as conclusive as that submitted the method should only be considered as an additional source of information. This is especially true, as samples of pure milk with less than the accepted minimum of total solids are found from time to time. Not many years ago 11.5 per cent of total solids would have been thought to indicate a watered milk, and now 11.38 is quoted by Mr. Leach. I have found that the sum of the gravity and the fat, as suggested by Richmond, gives a very accurate standard for indicating the presence of added water.

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[a] Method of Leach and Lythgoe.

REPORT ON TEA AND COFFEE.

By Hermann C. Lythgoe, *Associate Referee.*

During the past year no new investigation has been attempted and collaborative work could hardly be planned to advantage, since only one analyst offered his services, but the methods submitted at the last convention have been used with marked success in the laboratory of food and drug inspection of the Massachusetts State board of health for the approximate quantitative determination of the ingredients of samples of adulterated coffee.

It is not necessary to make a complete analysis of each sample, determinations of petroleum ether extract, crude fiber, reducing sugars, starch, and caffeine being as a rule sufficient for quantitative supplementation of the microscopic examination. Under certain conditions, however, it is desirable to know the ash, sand, chlorin, phosphates, cold water extract, and ten per cent extract.

Coffee has from 12 to 15 per cent of petroleum ether extract and from 1 to 1.4 per cent of caffeine. Adulterants of coffee have but little fat (none to 3 per cent) and no caffeine; therefore these two determinations are sufficient to ascertain the amount of coffee present. The presence of chicory will materially increase the reducing sugars, as there are from 18 to 20 per cent of reducing sugars in chicory and from 0.3 to 1.7 per cent in coffee. For determining the amount of roasted grains a starch determination is necessary. Roasted wheat has from 27 to 30 per cent of starch (a portion of the starch being caramelized during the process of roasting) while coffee has only from 1 to 3 per cent. A crude fiber determination is desirable when leguminous hulls are present. Occasionally it is advisable to know the amount of phosphates when cereals and legumes are present, and the cold water extract, sand, and chlorin if the coffee is adulterated with chicory.

Mr. McGill, the associate referee on cereal products, stated that he had no formal report to make, but desired to describe a method he had been using for the determination of the gluten content of flours. The method consists in the preparation of a solution of the gluten flour in a normal ammonia solution and the determination of the viscosity and surface tension of the resulting solution. It was found that these physical properties of the solution vary with the amount of gluten present in the flour.

Ten grams of flour are mixed with an equal amount of water and allowed to stand half an hour. The dough is shaken with normal ammonia and made up to a definite volume. The viscosity and surface tension of the resulting solution is then determined by means of a special 6 cc pipette, the end of which is ground to a smooth external surface so that a liquid will flow from it in drops of uniform size. The size of the drops is dependent upon the surface tension of the solution, so that the relative number of drops formed by the delivery of 6 cc of two different gluten solutions represents the relative amounts of gluten present in the flours from which the solutions were made. A stalagmometer patented in Germany was used in these investigations.

In the same way the viscosity of the solutions is determined by noting the number of seconds taken in the delivery of the 6 cc. Thus there are obtained measurements of viscosity in terms of seconds and of surface tension in terms of number of drops. Some flours give for viscosity measurements 228 seconds and others as low as 179 seconds.

For surface tension some give 62 drops for delivering 6 cc and others 42 drops. It is not yet certain from the limited amount of work done just what the full significance of these figures is, and Mr. McGill requested the cooperation of other workers along this line in the study and perfection of this method.

REPORT ON PRESERVATIVES.

By W. D. Bigelow, *Referee.*

The study of the effect of the process of canning on chemical preservatives added in the preparation of food has been continued. At the time of the preparation of the report presented at the last meeting of the association a number of products canned without preservatives and in the presence of known amounts of the various preservative chemicals had not yet been examined. These preparations have been taken up during the past year and the content of preservatives determined.

It was found that in no case where preservatives had not been employed was any reaction obtained which could possibly be interpreted as indicating the presence of chemical preservatives. This was true even in the case of canned goods which had been subjected for fifty minutes to a temperature of 250° F. under the pressure of steam at that temperature. Considerable difficulties attended the examination of goods canned after the addition of chemical preservatives because of the inaccuracy of the methods employed for quantitative determination of several of the preservative substances. It has been found in all cases, however, that the amount of preservatives found in the canned product was, within the limits of accuracy of the methods of analysis, identical with that added to the product before canning.

Detection of Formaldehyde.

The method of Arnold and Mentzel [a] (Bul. 90, p. 47, Method 5) for the detection of formaldehyde by means of ferric salts has been studied further, with results in general confirmatory of those reported a year ago. The method appears to be applicable to the detection of formaldehyde in solutions of from 1 part in 40,000 to 1 part in 50,000. This reaction is apparently characteristic for formaldehyde, as acetic aldehyde and benzaldehyde do not interfere.

The method by the same authors [b] (Bul. 90, p. 48, Method No. 6), using phenylene hydrazine hydrochlorid and sodium nitroprussid, has also been further studied. This result appears to be somewhat more delicate than the preceding method, and also to be a characteristic reaction for formaldehyde in the absence of an appreciable amount of other aldehydes. The presence of acetic aldehyde and benzaldehyde in appreciable quantities interferes with the reaction for formaldehyde by giving a yellowish or yellowish-green tinge, whereas in the presence of formaldehyde alone the color is pure green. The reaction for acetic aldehyde and benzaldehyde alone is red or brown, and can not be mistaken for formaldehyde.

The method of Rimini [c] (Bul. 90, p. 48, Method No. 7) for the detection of formaldehyde by means of ferric chlorid and sodium nitroprussid followed by concentrated hydrochloric acid was further studied and found to be satisfactory in the presence of formaldehyde in dilution of greater than 1 part in 40,000 or 50,000. While this method is less delicate than either of the two preceding, it also appears to be characteristic for formaldehyde.

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[a] Zts. Nahr. Genussm., 1902, *5:* 353.

[b] Chem. Zeit. 1902, *26:* 246; abs. J. Chem. Soc. 1902 (2) *82:* 367; abs. Chem. Centrbl., 1902, pt. 1, p. 1077.

[c] Ann. di Farmacol. 1898, p. 97; abs. Chem. Centrbl., 1898, pt. 1, p. 1152; abs. J. Soc. Chem. Ind., 1898, *17:* 697.

DETECTION OF BENZOIC ACID.

Considerable difficulty has been experienced for several years by the members of the association with Peter's method for the detection of benzoic acid. (Appendix Bul. 65, p. 160.) While some analysts reported no difficulty in detecting benzoic acid by this method, others were unable to get reactions with certainty when benzoic acid was known to be present. This method has been carefully studied during the past year by Mr. Charles S. Ash, who has compared as oxidizing agents for this purpose barium dioxid, ammonium persulphate, sodium dioxid, calcium dioxid, magnesium dioxid, and potassium percarbonate in the presence of sulphuric acid and hydrogen peroxid in solutions made alkalin with ammonia. His results are given in Table I.

TABLE I.—*Detection of benzoic acid after treatment with various oxidizing agents for twelve hours* (Ash).

Quantity of benzoic acid.	Barium peroxid.	Ammonium persulphate.	Sodium peroxid.	Calcium peroxid.	Magnesium peroxid.	Potassium percarbonate.	Hydrogen peroxid.[a]
Mg.							
10	Good	Good	Fair	Good	Good	Good	Good.
5	do	do	do	do	do	do	Do.
2	Red brown	Red brown	Nothing	Faint trace.	do	do	Do.
1	Trace, brown.	Trace, brown.	do	do	Faint, but clear.	do	Do.
½	Nothing	Nothing	do	Nothing [b]	Nothing	Faint, but clear.	Faint, but clear.

[a] Useless with hydrogen peroxid in acid oxidation; see special method described for oxidation in the presence of ammonia.
[b] Sometimes a faint reaction with one-half milligram is obtained.

Potassium permanganate, potassium chlorate, manganese dioxid, and lead peroxid are useless for this oxidation. It is apparent also that the first four reagents mentioned in the table are not as suitable for this method as the others, and that sodium peroxid is perhaps the least available of all. Good reactions are reported in the presence of 1 milligram of benzoic acid by the last three methods given, while with potassium percarbonate in the presence of strong sulphuric acid and with hydrogen peroxid in alkaline solution one-half milligram of benzoic acid was detected with certainty. Mr. Tolman confirmed this work with reference to magnesium peroxid, and obtained good results with that reagent. The following detailed description of the precautions necessary in the various methods has been given by Mr. Ash:

NOTES ON PETER'S METHOD, BY C. S. ASH, CALIFORNIA WINE ASSOCIATION.

For this method the wine is extracted by shaking with chloroform in a separatory funnel after acidifying with 5 cc of one-third sulphuric acid. The chloroform is allowed to evaporate to dryness in a small porcelain dish. When benzoic acid is present in considerable quantities the crystalline character of the residue frequently indicates its presence. The dish containing the residue is placed in a vessel of ice water, a few cubic centimeters of strong sulphuric acid are added, and the contents are then stirred until the residue is dissolved. Barium peroxid is then gradually dusted into the dish, with continual stirring, until the liquid begins to foam, after which a few cubic centimeters of commercial hydrogen peroxid are added, drop by drop. The dish is then taken from the water and its contents are diluted with water to convenient bulk, the barium sulphate is removed by filtration, and the filtrate, which should still be acid, shaken with chloroform. The chloroform extract is then tested for salicylic acid as directed in the method for the detection of salicylic acid. Doctor Peter also suggests that persulphate of ammonium affects this oxidation.[a]

Barium dioxid (BaO_2).

This test was conducted as described by Peter.

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[a] U. S. Dept. Agr., Division of Chemistry, Bul. 59, p. 60.

Table II.—*Oxidation of benzoic acid with barium dioxid.*

Amount of benzoic acid.	Barium dioxid.		Oxidized 12 hours with barium dioxid and then 12 with hydrogen peroxid.
	Oxidized ½ hour.	Oxidized 12 hours.	
Mg.			
10	Good	Good	Good.
5	Trace, red-brown	do	Do.
2	Nothing	Red-brown	Fair, red-brown.
1	do	(Poor) brown	Red-brown
½	do	Nothing	Darkens.

The time of oxidation seems to be quite a factor here. When the quantity is small, a purple reaction is not obtained, but a red-brown one, which justly may be taken for a negative reaction caused by organic matter.

Ammonium persulphate $[(NH_4)_2S_2O_8]$.

What has been said of the oxidation with barium dioxid applies also to ammonium persulphate. The latter, however, in the writer's opinion, is a little more sensitive.

Table III.—*Oxidation of benzoic acid with ammonium persulphate.*

Amount of benzoic acid.	Ammonium persulphate.		Oxidized 12 hours with ammonium persulphate and then 12 with hydrogen peroxid.
	Oxidized ½ hour.	Oxidized 12 hours.	
Mg.			
10	Good	Good	Good.
5	Fair, red-brown	do	Do.
2	Red-brown	Red-brown	Red-brown.
1	Nothing	Red-brown (poor)	Do.
½	do	Nothing	Darkens.

Sodium peroxid (Na_2O_2).

This reagent is too rapid in action and almost useless. A great amount of heat is evolved and oxidation can be obtained only at a very low temperature, and a very slow addition of sodium peroxid. In the presence of less than 5 milligrams of benzoic acid no reaction was obtained, and with that quantity the result was unreliable. Ten milligrams give a fair reaction.

Calcium peroxid (CaO_2).

This reaction is good but not delicate. All reactions obtained are purple, but never red brown. Two milligrams seem to be its limit of delicacy. The time of oxidation makes little difference.

Table IV.—*Oxidation of benzoic acid with calcium peroxid.*

Amount of benzoic acid.	Calcium peroxid.	
	Oxidized 1 hour.	Oxidized 12 hours.
Mg.		
10	Good	Good.
5	do	Do.
2	Trace	Trace.
1	Nothing	Rarely faint trace.
½	do	Nothing.

Magnesium peroxid (MgO_2).

This reagent is a great improvement over barium dioxid and ammonium persulphate, having the advantage of calcium peroxid and giving good results to 1 milligram

Table V.—*Oxidation of benzoic acid with magnesium peroxid.*

Amount of benzoic acid.	Magnesium peroxid.		Oxidized 12 hours with magnesium peroxid and then 12 with hydrogen peroxid.
	Oxidized 1 hour.	Oxidized 12 hours.	
Mg.			
10	Good	Good	No benefit.
5	do	do	
2	do	do	
1	Trace	Faint but clear	
½	Nothing	Doubtful	

Potassium percarbonate ($K_2C_2O_6$).

This is the best reagent for oxidation of benzoic acid to salicylic acid in accordance with Peter's method. Reactions were all clear purple, even to the faint traces. Time makes little difference.

Table VI.—*Oxidation of benzoic acid with potassium percarbonate.*

Amount of benzoic acid.	Potassium percarbonate.		Oxidized 12 hours with potassium percarbonate and then 12 with hydrogen peroxid.
	Oxidized 1 hour.	Oxidized 12 hours.	
Mg.			
10	Good	Good	No benefit.
5	do	do	
2	do	do	
1	Fair	do	
½	Trace	Faint but clear	

Table VII.—*Potassium percarbonate experiment to determine effect of quantity of sulphuric acid.*

Amount of benzoic acid.	12 hours oxidation.	
	10 cc sulphuric acid.	5 cc sulphuric acid.
Mg.		
5	Good	Good.
2	do	Do.
1	do	Do.
½	Doubtful	Good trace.

The amount of sulphuric acid is not particularly essential. Too large amounts, however, should be avoided.

Hydrogen peroxid (H_2O_2).

Hydrogen peroxid is useless in the acid oxidation, but is of great value when used in the presence of ammonia.

To the residue left by the solvent add 3 cc strong ammonia; then add 10 cc of hydrogen peroxid and pour into a test tube. Wash the dish with 15 cc more of hydrogen peroxid and put this also in the test tube. Shake, allow to stand for a few hours, make acid with sulphuric acid, extract with ether or chloroform, evaporate, and test as usual for salicylic acid.

TABLE VIII.—*Oxidation of benzoic acid with hydrogen peroxid in alkaline solution.*

Benzoic acid.	Hydrogen peroxid.	
	4 hours.	12 hours.
Mg.		
10	Good	Good.
5	do	Do.
2	do	Do.
1	do	Do.
½	Trace	Faint but clear.

This is equal to acid oxidation with potassium percarbonate and very much more simple to operate.

The work on preservatives also included a revision of the preservative methods published as Circular No. 28 of the Bureau of Chemistry.

DETERMINATION OF SOLIDS IN CIDER AND VINEGAR.

By J. A. LE CLERC and L. M. TOLMAN.

The work along this line has been been conducted for the most part by Smith,[a] Doolittle and Hess,[b] Frear,[c] Leach,[d] and Van Slyke.[e] Smith determined the solids by evaporating 5 to 10 grams in a flat-bottom dish to constant weight, in a water oven, and found that vinegars, except those made from early summer apples, contain from 2.5 to 4 per cent solids.

Leach exposed 5 grams of vinegar in a flat-bottom dish for 1 hour to direct contact with live steam of a boiling water bath. His results showed that only a few samples were below the Massachusetts standard of 2 per cent, from which it appeared that it was not too high for properly fermented cider vinegar, and therefore upheld the standard of 2 per cent solids. The results published in Bulletin 258 of the New York station were obtained by drying 5 grams of material on sand in a steam oven for 6 to 8 hours. From the work carried on at Geneva by Le Clerc in connection with Van Slyke, it appears that whereas the acid content in vinegar comes up to the legal standard of 4.50 per cent, when proper fruit is used, and conditions of fermentation are properly controlled, it is not possible always to produce vinegars containing 2 per cent of solids. Further, the failure to find 2 per cent of solids in vinegars is somewhat, though not wholly, due to defective methods of analysis or too long drying, as may be shown by the following figures obtained by Van Slyke:

The average of 22 samples analyzed for solids (1) by drying 1 hour over boiling water, was 2.18 per cent; (2) by drying to sirup and then drying 2½ hours in oven at 212°, was 2.14 per cent; and (3) by drying on sand 8 hours in steam oven, was 2.05 per cent.

Thus vinegars which on drying for 1 hour might yield the legal standard amount of solids, 2 per cent, would, if dried for 6 hours in a steam oven, give but 1.87 per cent solids, and therefore fall below the standard. According to Van Slyke, it would seem rather desirable to word the method of procedure so as to leave no doubt as to the time of evaporation, surface exposed, and the character of the drying apparatus.

The results obtained at Geneva show that out of 36 experiments in making vinegar from apples fully one-third were below the legal standard of 2 per cent solids, although over 4.5 per cent acid was found, and this no matter by what method of analysis the solids were determined. The solids of vinegar consist of glycerol, proteid material, gums, malic acid, and ash, and when we consider that levulose may still be present (as Browne has shown)[a] in small amounts in vinegar and that it is decomposed on heating, it would seem necessary to modify the method of drying ciders and vinegars so as to cause as little destruction of levulose and other bodies as possible. This can be done by drying in a vacuum oven at 70° for one to one and one-half days.

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[a] J. Amer. Chem. Soc., 1898, *20:* 4.

[b] J. Amer. Chem. Soc., 1900, *22:* 218.

[c] Pa. Dept. Agr., 1898, Annual Rept., p. 145; Bul. 58.

[d] J. Amer. Chem. Soc., 1904, *26:* 377.

[e] New York Agr. Exper. Sta., Bul. 258.

Inasmuch, however, as vacuum ovens are not in use in all laboratories, we have adopted a modification of Leach's method, i. e., of drying 5 to 10 grams of material in a flat-bottom dish 2 hours (instead of 1 hour) in direct contact with live steam. Thirty-eight different samples of cider and vinegar were dried for 2 hours on the steam bath, and likewise one day in a vacuum oven at 70°. The average solid content of samples dried on the steam bath for 2 hours was 4.01 per cent, in the vacuum oven 3.99 per cent. In 30 of the above samples the difference was 0.15 per cent or less. In only 8 samples was the difference more than 0.15 per cent, the maximum being 0.23 per cent.

It is therefore quite possible to obtain a correct estimation of solids in ciders and vinegars by drying these substances in a flat-bottom evaporating dish in a live steam bath for 2 hours. That it is necessary to evaporate for 2 hours is shown from the fact that Van Slyke obtained almost identical results when using the provisional method[b] and when drying his sample one hour over live steam, as Leach suggested.

Our results showed that 2 hour's drying give somewhat lower results than 1 hour's drying. For example, 10 samples dried for 1 hour gave an average of 3.08 per cent. The same when dried 2 hours gave 2.87 per cent. When these figures were compared with those obtained in the vacuum oven it was found that the latter agreed most closely with the results obtained on drying for 2 hours.

THE LEAD PRECIPITATE TEST FOR MALIC ACID.

By L. M. Tolman and J. A. Le Clerc.

In the Provisional Methods for the Analysis of Foods[c] the following statement is made:

> The presence of malic acid distinguishes cider vinegars, though the quantity is often small. Failure to obtain a precipitate upon the addition of a few drops of neutral lead acetate to 10 cc of a vinegar, proves it not to be cider vinegar; if a precipitate be obtained, parallel tests with silver nitrate and barium chlorid to determine the absence of chlorids and sulphates should be made, before the presence of malic acid be considered proved.

This qualitative test is used to a great extent to determine the purity of cider vinegar, being an easy and quick method. The following facts have led us to question whether the reaction is due to the presence of malic acid:

(1) The seemingly incontrovertible fact that lead malate is soluble to a very considerable extent in 4 per cent acetic acid. Much higher percentages of malic acid must be present than ever occur in cider vinegar to give a precipitate with lead in a 4 per cent acetic acid solution.

(2) Some pure cider vinegars prepared by Mr. Alwood, of the Virginia Experiment Station, showed only a trace of fixed acids present and yet gave a most voluminous precipitate with lead acetate.

(3) The lead precipitate from a cider vinegar prepared in this laboratory was collected and thoroughly washed, the lead removed by hydrogen sulphid, the excess of hydrogen sulphid removed by boiling, and the solution neutralized with sodium hydroxid, evaporated to dryness, and ashed. This ash did not effervesce on the addition of acid, indicating that no organic acid had been present, and it was found on analysis to contain sufficient phosphoric acid (P_2O_5) to account for over 80 per cent of the ash, indicating that the chief component of the precipitate is lead phosphate, which carries down what tannin there may be

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[a] J. Amer. Chem. Soc., 1903, *25:* 16.

[b] U. S. Dept. Agr., Bureau of Chemistry, Bul. 65, p. 63.

[c] Loc. cit., p. 68.

present and some of the coloring matter. Considerable amounts of sulphates were also found.

The vinegar which had been treated with lead was treated with hydrogen sulphid to remove the excess of lead, boiled to remove the hydrogen sulphid, evaporated, and ashed. An examination of this ash showed that all but the merest trace of phosphoric acid had been removed. It would appear, therefore, that this is not a test for malic acid, but for phosphoric acid, and the following change is recommended:

That the following words in Bulletin 65, page 68, beginning with the twenty-fourth line, be eliminated: "The presence of malic acid distinguishes cider vinegars, though the quantity is often small. . . . . . If a precipitate be obtained, parallel tests with silver nitrate and barium chlorid to determine the absence of chlorids and sulphates should be made before the presence of malic acid be considered proved."

SECOND PRESSING CIDER.

By L. M. Tolman and J. A. Le Clerc.

The second-pressing cider was prepared by pressing the pomace which had been allowed to ferment in large heaps for from ten days to two weeks, or even more. During this time the fermentation is quite active. The heap of pomace becomes very hot and gives off a strong odor of acetic acid, showing that alcoholic and acetic fermentations at least are in progress, and it is probable that other fermentations are going on as the conditions are suitable.

The composition of this second-pressing cider is extremely interesting. The analysis, which was made as soon as possible, showed in a typical sample 3.32 per cent of alcohol and 6.44 per cent of solids, indicating about 14 per cent of solids in the original juice, 9.50 per cent of sugar, and 4.5 per cent of nonsugar solids, as against 14.50 per cent of solids in the first-pressing cider, 11.5 per cent of sugar, and 3 per cent of nonsugars.

During the fermentation this difference becomes much more marked, as the first-pressing cider contains 0.6 per cent of malic acid which disappears in the fermentation, while the second pressing contains a fixed acid which does not ferment, but the amount actually increases as the fermentation proceeds. The chief point of difference, however, is in the composition of the nonsugar solids left after the fermentation of the sugar is complete. This amounts to 4.5 per cent in the second-pressing cider and about 1.8 per cent in the first pressing.

It was found that of this 4.5 per cent about 0.5 per cent was nonvolatile acid, 0.8 per cent was pentosans, and 1.5 per cent was precipitated by alcohol. An analysis of this alcohol precipitate by H. C. Gore showed it to contain approximately 46 per cent of galactans and 33 per cent of pentosans. Mr. Gore also showed that only about 60 per cent of the pentosans were precipitated by alcohol, so that 1.8 per cent of the solids of this cider consists of pentosans plus alcohol precipitate. The total galactans in the cider were not estimated. The first-pressing cider contained only traces of pentosans and alcohol precipitate. The amount of ash was also much higher.

One of the most striking differences is in the fixed acids, which increase during the fermentation instead of decreasing, as in the case of the first-pressing cider. This is due, perhaps, to the formation of lactic acid, which forms readily under the conditions of fermentation present in the pile of pomace.

Another peculiar fact is that in the polarization of the cider before and after inversion there is a slight increase in the right hand reading and also an increase in the amount of reducing substances, showing that some of the gums or similar bodies present are easily hydrolized. This increase in reducing sugars can not be due to cane sugar, as in that case the polarization would have been increased to the left.

All these facts indicate that in second-pressing cider prepared from pomace treated in this way we have a very different product from that prepared by pressing the juice from the freshly-ground apple, and it seems likely that the addition of this to first-pressing cider can be readily detected.

Mr. R. F. Hare, of the New Mexico station, called attention to the opuntia, a fruit of that region used extensively as a food by the Mexicans, showing samples of the fruit and jellies prepared from it. Some of the fruits are over half a pound in weight and very sweet, containing 12 per cent of sugar and having also the cactus flavor, of which many are very fond. In cooking the fruit the pericarp, which is from one-eighth to one-half of an inch thick, is also eaten. The samples were collected in New Mexico, Arizona, and old Mexico, and a complete study of the composition of the fruits and their various products is being made by Mr. Hare in connection with the Bureau of Plant Industry of the Department of Agriculture. Doctor Bigelow spoke of the value of such investigations in making known the composition of tropical fruits by work done in the region of growth, unsuccessful efforts having been made to complete the study on the ripening of fruits made in the Bureau of Chemistry on apples, peaches, oranges, and persimmons by studies of tropical fruits, as the changes in composition en route rendered the work futile.

Doctor Bigelow further called attention to the demands for household or simple tests for the detection of food adulterants, made by both housekeepers and dealers, and suggested that a special meeting of the food chemists be held to discuss the subject after the adjournment of the association at 4 o'clock. Mr. McGill stated that the same demand was often made by the Canadian dealers, claiming that they could not tell whether a baking powder, for instance, was pure or not, and that he had some simple apparatus for this purpose, the use of which he would explain at the proposed special meeting.

Doctor Frear, referring to the paper presented by Mr. Howard on microscopic tests for foreign starches in cocoa, spoke at some length in regard to a sample of cocoa which was condemned on the basis of the form, size, and quantity of the large-sized grains present, and the case taken into court. Further examination showed that the swelling of the cocoa grain was such when placed on the slide with a drop of water and subjected to heat that the distinction between the cocoa and the wheat starch grains could not be made. This case was the one referred to in Mr. Howard's paper as furnishing the suggestion for his investigation.

Mr. Cochran stated that he examined the same sample which was subsequently submitted to Mr. Frear and failed to discover any appearance of foreign starch grains. Subsequently the speaker examined six samples of roasted cocoa beans from different factories, using the polariscope in addition to the ordinary illumination, and still failed to find any resemblance to foreign starch grains in the pure product of the cocoa bean.

REPORT ON MEAT AND FISH (DETERMINATION OF SOME NITROGENOUS CONSTITUENTS OF FLESH).

By M. E. Jaffa, *Associate Referee.*

Two samples were made of raw meat as follows: 665 A, by means of sausage machine, meat put through three times; 666 B, meat treated in mortar, ground as fine as possible. The analyses of these samples were as follows:

Table I.—*Analyses of raw meat.*

Determination.	Sample No. 665.	Sample No. 666.
	Per cent.	*Per cent.*
Water	75.35	74.73
Protein	21.89	21.70
Fat	1.87	.88
Ash	1.13	1.20
Total	100.24	98.51

The figures reported are averages of duplicates. The lower content of fat in No. 666 is probably due to the fact that the sample was not as well prepared as No. 665. The same is probably true of the figure for the water, as both determinations were made under identically the same conditions.

Table II.—*Results of analyses of cold-water extract.*

Determination.	Sample No. 665.	Sample No. 666.
	Per cent.	*Per cent.*
Total solids	5.47	5.57
Total ash	1.12	1.18
Total acidity	.38	.38
Coagulable proteids	2.02	2.16
Albumoses	.38	.27
Peptones	.08	.22
Flesh bases	1.16	.91

Table III.—*Results of analyses of 10 per cent sodium-chlorid extract.*

Determination.	Sample No. 665.	Sample No. 666.
	Per cent.	*Per cent.*
Proteids coagulated by heat	4.07	4.03
Proteids precipitated by acid in filtrate	.71	.80
Proteids precipitated by zinc sulphate	.33	.36
Proteids precipitated by bromin	.10	.14
Proteids not precipitated by above reagents	.10	.06
Total	5.31	5.39
Total by direct action	5.40	5.48

Treatment with 0.15 per cent hydrochloric acid gave soluble proteids for No. 665, 1.90 per cent; for No. 666, 1.77 per cent; with 0.15 per cent potassium hydrate the result for No. 665 was 5.70 per cent, for No. 666, 6.60 per cent. The residual proteids, direct determination, were for No. 665, 2.28 per cent, for No. 666, 2.60 per cent.

TABLE IV.—*Nitrogen balance.*

Determination.	Sample No. 665.	Sample No. 666.
	Per cent.	*Per cent.*
In cold-water extract	0.7712	0.7140
In 10 per cent sodium chlorid	.8640	.8768
In 0.15 per cent hydrochloric acid	.3040	.2832
In 0.15 per cent potassium hydrate	.9120	1.0560
In residue	.3648	.4160
Total	3.2160	3.3460
Direct determination	3.5024	3.4720
Loss	.2864	.1260

REPORT ON DAIRY PRODUCTS.

G. E. PATRICK, *Referee.*

Following the instructions of the association, the two lines of work reported upon at the last meeting have been made the subjects of further study the past year. They are (1) The Effects of Preservatives upon the Determination of the Proteids of Milk, and (2) Methods for the Detection of Renovated Butter. The third subject recommended, viz, Methods of Determining Sugars in Condensed and Dried Milks, your referee has not been able to take up for systematic study.

1. EFFECTS OF PRESERVATIVES UPON THE DETERMINATION OF THE PROTEIDS OF MILK.

In a circular letter sent out early in September the following preservatives, in the amounts stated, were recommended for trial this year, the amounts to be used being slightly changed from those of last year:

		Per liter of milk.
Formalin (40 per cent strength)	(*a*)	1.5 cc.
	(*b*)	3.0 cc.
	(*c*)	4.5 cc.
	(*d*)	8.0 cc.
Chloroform		50.0 cc.
Mercuric chlorid, in impalpable powder	(*a*)	1.0 gram.
	(*b*)	2.5 grams.
	(*c*)	5.0 grams.
Potassium bichromate, saturated aqueous solution	(*a*)	10.0 cc.
	(*b*)	20.0 cc.
Carbon bisulphid		20.0 cc.
Benzol		50.0 cc.
Sodium fluorid		20.0 grams.

The following suggestions were also made:

The milk should be fresh and well skimmed—at least it should not contain very much fat, as this makes sampling difficult. The analyses, for both casein and albumin by association methods, should be made on the fresh milk before the addition of preservatives, on the preserved milk after about 18 days, and if possible again after about 34 days. (These periods of examination were observed in the work of 1904.) It would be well also, if time should permit, to analyze the fresh milk immediately after the preservatives have been added.

The results obtained must of course be corrected for volume where liquid preservatives are used.

State or indicate by their association names the methods of determination employed.

This letter was sent to all members of the association known to be specially interested in dairy work, but reports (on the preservative work) have been received from workers in only two laboratories. The collaborators were Frederick Kenney, Department of Health, New York City; F. W. Woll and George A. Olson, Agricultural Experiment Station, Madison, Wis.; G. E. Patrick and T. C. Trescot, Department of Agriculture, Washington, D. C.

REPORT OF MR. KENNEY.

The casein was determined by the official method, and the albumin by the provisional method.

TABLE I.—*The effect of preservatives upon the determination of milk proteids* (*Kenney*).

Kind and amount of preservative used.	Number of days elapsing before analysis.	Nitrogen of casein.	Nitrogen of albumin.	Nitrogen of casein and albumin.
		Per cent.	*Per cent.*	*Per cent.*
None, fresh milk	None.	0. 411	0. 049	0. 460
Formalin (about 40 per cent), 1.5 cc per liter	18	. 410	. 049	. 459
	34	. 409	. 047	. 456
Formalin, 3.0 cc per liter	18	. 419	. 047	. 466
	34	. 423	. 045	. 468
Formalin, 4.5 cc per liter	18	. 461	None.	. 461
	34	. 472	None.	. 472
Formalin, 8.0 cc per liter	18	. 463	None.	. 463
	34	. 475	None.	. 475
Chloroform, 50 cc per liter	18	. 313	. 066	. 379
	34	. 301	. 058	. 359
Mercuric chlorid, 1 gram per liter	18	. 421	. 035	. 456
	34	. 428	. 031	. 459
Mercuric chlorid, 2.5 grams per liter	18	. 441	. 030	. 471
	34	. 439	. 028	. 467
Mercuric chlorid, 5.0 grams per liter	18	. 446	. 026	. 472
	34	. 452	. 023	. 475
Potassium bichromate, saturated solution, 10 cc per liter	18	. 341	. 048	. 389
	34	Coagulated.		....
Potassium bichromate, saturated solution, 20 cc per liter	18	. 338	. 046	. 384
	34	Coagulated.		....
Carbon bisulphid, 20 cc per liter	18	. 432	. 054	. 486
	34	. 431	. 045	. 476
Benzol, 50 cc per liter	18	. 342	. 053	. 395
	34	. 339	. 055	. 394
Sodium fluorid, 20 grams per liter	18	. 338	. 066	. 404
	34	Coagulated.		....

Remarks by referee.

Mr. Kenney has informed the referee verbally that in precipitating the albumins he did not heat the liquid to the temperature of boiling water, as is specified in the official directions, but merely heated on the steam bath until the precipitation was thought to be complete, usually about one-half hour, he estimates. The query arises whether this departure from the text of the method would impair the accuracy of the results.

According to the table, the best preservative was formalin, 1.5 cc per liter. With it the results after 18 and 34 days agreed almost perfectly with those upon the fresh milk. Not quite as good was the dose of 3 cc of formalin per liter; even with this very moderate amount the effect of an "excess" of formaldehyde seems to appear in the slightly increased "casein" and diminished albumin. The next two in order of merit appear to be mercuric chlorid, 1 gram per liter, and carbon bisulphid, 20 cc per liter; but neither of these was satisfactory. All of the others were positively unsatisfactory, either because of shortage of albumin by reason of precipitation of a part thereof with the casein—e. g., formalin, 4.5 and 8 cc per liter, and mercuric chlorid, 5 grams per liter—or because of a loss of casein, *but not of albumin*—e. g., chloroform, 50 cc; potassium bichromate solution, 10 and 20 cc; benzol, 50 cc; sodium fluorid, 20 grams per liter. In their general indications these results agree remarkably well with those obtained last year by other workers.

The work on the effect of preservatives upon the determination of albumin of milk was conducted in accordance with your circular letter of September 5. The official method was used for the determination of casein and the provisional optional method[a] for the determination of albumin. The separator skim milk used in these experiments was fresh from the university dairy barn, and the samples were kept throughout the experiment at room temperatures, 22° to 25° C. Corrections for the volume of preservatives added were made whenever necessary. You will notice from our results that neither the saturated solution of potassium bichromate nor chloroform prevented decomposition of the casein and that with 20 grams sodium fluorid and 1 gram of mercuric chlorid the results for casein are practically identical with those on the original milk. There is, however, an unaccountable loss of albumin nitrogen in these two samples. The remaining samples contained an increased amount of caseo-nitrogen at the end of the 18 and 35 day periods. The loss of nitrogen of the casein and albumin in the potassium bichromate and chloroform samples was undoubtedly due to enzymic action. Our results show that there is no difference in the percentages of caseo-nitrogen for the 18 and 35 day periods, except where the preservatives added did not inhibit proteolysis.

Analysis of original sample of skim milk.

	Per cent.
Total nitrogen	0.57
Nitrogen of casein	.422
Nitrogen of albumin	.094
Nitrogen of casein and albumin	.516

TABLE II.—*Effect of added preservatives upon the determination of milk proteids* (*Woll and Olson*).

Amount of preservative used per liter of milk.	18 days.			35 days.
	Nitrogen of casein.	Nitrogen of albumin.	Nitrogen of casein and albumin.	Nitrogen of casein.
10 cc saturated potassium bichromate[a]	0.350	0.071	0.421	0.275
20 cc saturated potassium bichromate	.391	.076	.467	.357
50 cc chloroform	.383	.026	.409	.312
20 cc carbon bisulphid	.461	.039	.500	.458
20 grams sodium fluorid	.435	.055	.490	.415
1 gram mercuric chlorid	.413	.067	.480	.405
2.5 grams mercuric chlorid	.456	.054	.510	.460
5 grams mercuric chlorid	.506	.011	.517	.504
1.5 cc formalin	.446	.057	.503	.347
3 cc formalin	.467	.053	.520	.470
4.5 cc formalin	.479	.047	.526	.468
8 cc formalin	.492	.040	.532	.490

[a] Ten cc saturated solution of potassium bichromate changed from chromic to chromous compound in 15 days.

Remarks by referee.

In this work not one of the preservatives proved satisfactory, even for a period of 18 days. In every case the albumin nitrogen fell short. This shortage, in the samples preserved with 3 cc or upward of formalin or with 2.5 grams or upward of mercuric chlorid, was caused by precipitation of some of the albumin along with the casein, while in all the other samples it was undoubtedly caused wholly or in part by enzymic action. The most striking instance of this latter kind—one without a parallel in last year's work or this—is the sample preserved with 50 cc of chloroform per liter, which, while suffering in 18 days a loss of about one-tenth its original casein, showed also a loss of almost three-fourths of its albumin. Less striking instances are the bichromate samples, which in 18 days lost 7 to 17 per cent of their casein and 20 to 25 per cent of their albumin. These instances contradict one general result of last year's work, which indicated that albumin is as a rule better protected from proteolytic change than is casein by those agents that do not protect perfectly. The carbon bisulphid sample appears to exemplify both kinds of change above mentioned, viz, an increase of "casein" by precipitation of some albumin with the true casein, and also an actual destruction of albumin by enzymic action, this last, however, being very small, only 0.016 per cent of albumin nitrogen, and perhaps due to mere error of analysis.

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[a] The details of procedure followed by Messrs. Woll and Olson in the precipitation of albumin are given on page 99, having been furnished in a later communication upon request of the referee.

RESULTS OF MESSRS. PATRICK AND TRESCOT.

After our work was under way it was learned that the (separated) milk used in the experiments had before separating been heated in a continuous pasteurizer to 160° F. While this treatment probably weakened to some extent the activity of the milk enzymes, it did not by any means destroy them, as was proved by the strong reaction obtained with Storch's test on the preserved samples, and as without this proof would have been known from the work of Babcock and Russell upon this subject.[a]

Moreover, an untreated portion of the milk used in the experiments of Series A was observed to be curdled within 24 hours in the laboratory; that used in Series B was not noticed. These facts, together with the scantiness of time then available for the work, led to the decision to continue the experiments with the pasteurized milk.

The experiments with formaldehyde constituted one series (A), those with all the other preservatives another (B), the two series being started a few days apart.

The official method was followed in determining the nitrogen of casein and the provisional method for the nitrogen of albumin. In this latter determination the liquid was actually boiled for about ten minutes to insure complete coagulation of the albumin; and in order to secure clear filtration of the albumin, 3 cc of alumina cream were added to the (cold) liquid just before filtering. Results were of course corrected, when necessary, for the volume of preservatives added.

TABLE III.—*Effect of added preservatives upon the determination of milk proteids* (*Patrick and Trescot*).

SERIES A. TRIALS WITH FORMALIN OF ABOUT 36 PER CENT FORMALDEHYDE.

Preservative added per liter of milk.	Days elapsing before analysis.	Nitrogen of casein.	Nitrogen of albumin.	Sum of casein and albumin nitrogen.	Nitrogen of albumoses and peptones.[a]	Sum of all determined.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
None—fresh milk	None.	0.464	0.091	0.555	0.008	0.563
Formalin, 1.5 cc	22	.463	.067	.530	.023	.553
Formalin, 3.0 cc	23	.475	.050	.525	.025	.550
Formalin, 4.5 cc	22	.490	.045	.535	.018	.553
Formalin, 8.0 cc	24	.499	.037	.536	.012	.548

[a] Precipitated in filtrate from albumin by phosphotungstic acid.

The time at our disposal did not permit of continuing the trials over longer periods, but the figures obtained suffice to show that excessive amounts of formaldehyde cause the results for casein to come too high and those for albumin too low, in this respect confirming the results of last year's work. Each figure for casein and albumin nitrogen is the mean of three or four closely concordant determinations. One and one-half cubic centimeters of formalin gave the best results, but was not quite satisfactory, the albumin falling a little low.

The formation of albumoses and peptones was, practically speaking, prevented by the largest dose of formalin and perhaps by the two largest, while with the smaller doses some proteolytic action certainly occurred. With the largest dose of formalin especially the writer is unable to account for the apparent loss of about 0.02 per cent of nitrogen of casein and albumin combined. Since no such loss in presence of the larger doses of formalin is shown by the work of the other two laboratories, some error in our work is naturally to be suspected here.

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[a] Wis. Agr. Ex. Sta., 15th Ann. Rep. (1898), pp. 82 and 84.

Table IV.—*Effect of added preservatives upon the determination of milk proteids* (*Patrick and Trescot*).

SERIES B. TRIALS WITH CHLOROFORM, CARBON BISULPHID, BENZOL, POTASSIUM BICHROMATE, POTASSIUM FLUORID, AND MERCURIC CHLORID.

Preservative added per liter of milk.	Days elapsing before analysis.	Nitrogen of casein.	Nitrogen of albumin.	Sum of casein and albumin nitrogen.	Nitrogen of albumoses and peptones.[a]	Sum of all determined.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
None—fresh milk	None.	0.463	0.098	0.561	0.012	0.573
Chloroform, 50 cc	30	.431	.067	.498	.075	.573
Carbon bisulphid, 20 cc	21	.499	.061	.560	.019	.579
Benzol, 50 cc	32	.367	.094	.461	.096	.557
Potassium bichromate, 50 cc of saturated solution	32	.416	.094	.510	.055	.565
Potassium fluorid, 20 grams	32	.414	.102	.516	.041	.557
Mercuric chlorid, 1 gram	22	.412	.112	.524	.038	.562
Mercuric chlorid, 5 grams	22	.507	.055	.562	.002	.564

[a] Precipitated in filtrate from albumin by phosphotungstic acid.

The total nitrogen content of this milk was 0.590 per cent.

Each nitrogen figure in Table IV is the mean of from two to four closely agreeing determinations, except the last figure for albumose and peptone nitrogen (0.002) which was determined by the Kjeldahl method on the very small precipitates from four determinations mixed together. The figures are not strictly comparable among themselves because the times of keeping varied from 21 to 32 days, but they show conclusively that not one of these preservatives, in the quantities used, can be relied upon for enabling the chemist to get true results for casein and albumin on milk samples preserved therewith for the times stated.

Examining the results in detail, it is seen that in the preserved milk albumin fell distinctly low only with mercuric chlorid in excess (5 grams), where more than one-third of it was carried down with the casein; with carbon bisulphid, where apparently the same action took place to a much smaller extent; and with chloroform, where there was a distinct loss of casein as well as of albumin, doubtless from action of the milk enzymes.

With benzol it was quite different. Here the albumin was preserved practically without loss for 32 days, while more than one-fifth of the original casein was lost. Entirely similar though less striking results were obtained with potassium bichromate, potassium fluorid, and the smaller dose of mercuric chlorid (1 gram), in all of which cases the albumin suffered no appreciable loss (if, indeed, any at all), while the casein lost about one-ninth of its original amount.

Of the earlier products of proteolysis, namely albumoses and peptones, the largest amount was found in the benzol sample, and lesser amounts in the chloroform, bichromate, and other samples in the exact order in which the total nitrogen of casein and albumin suffered loss. Proteolysis was entirely prevented by the larger dose of mercuric chlorid (5 grams) and very nearly prevented by 20 cc of carbon bisulphid—the latter during only 21 days, however.

DISCUSSION OF THE RESULTS AS A WHOLE.

Considering the results from the three laboratories as a whole, the most important fact shown is that not one of the preservatives studied kept the proteid constituents of milk, even for 18 to 22 days, in condition for accurate quantitative determination. In short, not one was found efficient. The least inefficient, for the time stated, was formalin at the rate of 1.5 cc per liter of milk. This was one of the two which last year were found "reasonably satisfactory." The other, carbon bisulphid, 20 cc per liter, was this year far less satisfactory, showing as it did a decided tendency to yield an excess of "casein" at the expense of albumin.

This year's work fully verified that of last in showing that excessive quantities of either formalin or mercuric chlorid (of formalin 3 cc or upward, of mercuric chlorid 2.5 grams or upward per liter of milk) will cause a part of the albumin to be precipitated with the casein. As just mentioned, carbon bisulphid this year evinced the same tendency.

The better preservation of albumin than of casein by the inefficient preservatives—meaning thereby those which allow some proteolytic action to go on but not those which cause a precipitation of albumin with the casein—is not evident to nearly so great an extent as it was in last year's work. In fact, in this year's report from the Wisconsin laboratory there is no evidence of it whatever, whereas in that of last year it was plainly shown in nearly every instance where casein suffered loss. It is, however, exhibited in Mr. Kenney's results this year on the samples preserved with chloroform, potassium bichromate, benzol, and sodium fluorid, and in the referee's results upon those preserved with bichromate, benzol, potassium fluorid, and the smaller dose of mercuric chlorid, not, however, upon that preserved with chloroform, although last year the chloroformed sample showed it plainly.

These contradictory results are probably to be explained, if at all, in different ways. Those from the same laboratory in different years, if obtained by exactly the same method of working, can perhaps be most justly referred to a difference in the proportions of different enzymes in the milks, or possibly to different temperatures of the room in which the samples were kept. These same supposed causes, if real, may have led to different results the present year in the three laboratories, but, as far as albumin is concerned, the discrepancies noted seem to find adequate cause much nearer at hand, in the different ways of carrying out the determination in the different laboratories—even aside from the fact that pasteurized milk was by mistake used in the Department laboratory.

The "provisional" method for albumin (Bul. 46, revised, p. 55) is evidently the only method intended to be used upon the filtrate from casein by the "official" method. It directs to neutralize the acid in the filtrate from casein, then to add 0.3 cc of 10 per cent acetic acid and heat to the temperature of boiling water for from 10 to 15 minutes, to filter, wash, and determine nitrogen.

The details followed in the three laboratories are here shown side by side. The casein was in all three laboratories precipitated by the "official" method, viz, 1.5 cc of 10 per cent acetic acid at 40° to 42° C.

Treatment of the filtrate from casein.

New York Board of Health Laboratory.	Wisconsin Experiment Station Laboratory.	Department of Agriculture Dairy Laboratory.
It was neutralized, treated with 0.3 cc of 10 per cent acetic acid, then heated on the steam bath until precipitation was thought to be complete, "probably about one-half hour usually."	Without being neutralized, it was "treated with 0.3 cc of 10 per cent acetic acid, and boiled down to about one-half its volume. This was then made up to the original volume with distilled water and boiled again, this process being repeated three or four times, until a clear break was observed. The albumin was then filtered and the filtrate therefrom again boiled to determine whether all the albumin had been precipitated, and was also tested by neutralizing with sodium hydroxid to make sure that no precipitate would appear."	It was neutralized, treated with 0.3 cc of 10 per cent acetic acid, heated on the steam bath and when hot placed over a flame and *boiled* for about ten minutes, until the liquid cleared by coagulation and cohesion of the albumin. After cooling, and just before filtering, 3 cc of well-washed alumina cream was added to insure perfect filtration.

In these different modes of treatment as to acidification, temperature of heating, and the length of time heating was continued—this last especially in view of the different degrees of acidity—your referee sees abundant cause for many of the discordant results reported in this year's work. In his opinion there is danger of too low results by merely heating on the steam bath for one-half hour, perhaps from incomplete precipitation, and surely from imperfect filtration unless some substance of the nature of alumina cream be used. And to boil for so long a time, especially with so much free acid present as is reported from the Wisconsin laboratory, seems to the referee, in the absence of comparative experiments, a procedure likely to give low results. As to his own innovation in the Department laboratory, viz, the adding of alumina cream to the cold liquid in order to insure complete retention of the albumin, he has not yet seen any objection to it, provided the cream be free of aluminum salts and of ammonia. If there be danger in its use, he would be glad to learn of it in order to avoid error in the future.

2. Methods for the Detection of Renovated Butter.

The directions for work were printed in Circular No. 19, revised, of the Bureau of Chemistry, and sent out with samples of butter to six persons who had expressed willingness to join in the work. To each person four samples of butter were sent, representing ordinary creamery, dairy, pasteurized, and renovated butters.

The dairy butter was of known purity, being made at a near-by dairy and duly authenticated. It was made from gravity cream, skimmed after the milk was curdled, the churning being done only once a week. The butter had, even when fresh, a decidedly over-ripe flavor. The pasteurized butter was made by a local dairyman, from cream which had been run through a continuous pasteurizer at 160° F. It was colored and salted to the degree usual for the Washington market. The creamery and renovated butters were purchased in the open market and were entirely typical of their kind.

Results were reported from four laboratories. The workers were Frederick Kenney, New York City Board of Health; F. D. Simons, United States Treasury Department, Washington, D. C.; F. W. Woll and George A. Olson, Wisconsin Agricultural Experiment Station, Madison; G. E. Patrick, Bureau of Chemistry, Department of Agriculture, Washington, D. C.

THE MELTING TEST.

The results by this test are given in the following table:

Table V.—*Melting test: Butter melted, without agitation or mixing, in boiling water oven; appearance of fat after one-half hour to one hour in oven.*

Observer.	1981. Creamery.	1982. Dairy.	1983. Pasteurized.	1984. Renovated.
Frederick Kenney	Clear	Clear	Clear	Turbid.
F. D. Simons	do	Slightly cloudy	Slightly cloudy	Do.
F. W. Woll and George A. Olson.	do	Clear	do	Do.
G. E. Patrick	do	do	Clear [a]	Densely turbid.

[a] Clear when melted in the boiling water oven, but turbid or very cloudy when melted at 60°–70° C., the temperature at which clearer melts have sometimes been obtained with old butters.

These results are all in practical agreement, since the slight cloudiness reported in some instances with the dairy and the pasteurized butter could not be mistaken for the turbidity of the renovated. The referee found that this sample of pasteurized butter, while yielding a clear fat when heated in the boiling water oven, gave a very cloudy or even a turbid fat when melted at 60°–70° C. From this and other observations he concludes the temperature of 60°–70°, mentioned in Circular No. 19 as the temperature yielding the clearest results with rancid butters, is too low and that the temperature of the boiling water oven is decidedly preferable. But it is advised to place the tubes on a shelf or other support in the oven, and not directly in contact with the bottom, where the heat is the greatest, as this is apt to cause mixing in the tubes by convection.

THE BOILING OR FOAM TEST.

Table VI.—*The boiling test, using test tube or spoon.*

Observer.	Method.	1981. Creamery.	1982. Dairy.	1983. Pasteurized.	1984. Renovated.
Frederick Kenney	Tube	Some noise, little foam.	Quietly, with foam.	Quietly, with abundant foam.	Noisily, rushing sound, no foam.
	Spoon	Quietly, with foam.	do	do	Sputters, no foam.
F. D. Simons	Tube	Quietly, foam scanty.	Quietly, foam moderate.	Quietly, foam abundant.	Bumps and boils noisily, no foam.
	Spoon	Quietly, foam abundant.	Quietly, foam abundant.	do	Sputters; no foam.
F. W. Woll and George A. Olson.	Method not stated.	Quietly, much foam.	Crackling, some foam.	Quietly, much foam.	Crackling, some foam.
G. E. Patrick	Tube	Quietly, abundant foam.	Rushing sound, very abundant foam.	Quietly, very abundant foam.	Noisily, loud rushing sound, a little crackling, no foam.
	Spoon	Some sputtering, abundant foam.	A little sputtering and crackling, very abundant foam.	A little sputtering, abundant foam.	Much sputtering; no crackling, no foam.

The results by the boiling test are in nearly all cases in practical agreement as regards the most important feature of the test, namely, the amount of foam. It is evident from the results that a better judgment can be obtained by the use of both forms of the test than by either one alone, especially in the hands of a person not experienced in this work, and it is the referee's custom to employ both forms in all difficult cases. This point is illustrated in the results of Messrs. Woll and Olson. These observers report only one set of observations, not stating by which method, and from the results reported one could only conclude that samples 1982 and 1984 were substantially the same kind of butter. The writer can not understand how observations so nearly alike as to be reported in identical words could be obtained on these two butters, a dairy and a renovated, by either of the methods, and it is almost certain that if both methods had been employed some difference would have been observed and reported. This conclusion is justified by a study of other reports in the table.

MICROSCOPIC EXAMINATION.

Only two workers reported upon this part of the work.

Table VII.—*Microscopic examination.*

NO. 1981. CREAMERY BUTTER.

Observer.	Light field.	Dark field.	Polarized light, crossed nicols.	Polarized light, with selenite plate.	Melted on slide at 60°-70° C. Appearance of curd.
F. D. Simons	Fairly smooth; moderate amount of casein, dirty yellow, dry.	Casein gelatinous	Slight haziness		Fleecy or moss-like straggling forms.
G. E. Patrick	Smooth; no casein.	Nothing	Nothing, save an occasional "fairy ring."[a]	Nothing	All in moss-like forms.

NO. 1982. DAIRY BUTTER.

Observer.	Light field.	Dark field.	Polarized light, crossed nicols.	Polarized light, with selenite plate.	Melted on slide at 60°-70° C. Appearance of curd.
F. D. Simons	Smooth; scanty casein, pale yellow, dry.	Casein gelatinous.	Marked haziness.		Fleecy or moss-like straggling forms.
G. E. Patrick	Nearly smooth; few casein spots, small pale yellow, dry.	Many very minute casein spots now visible, gelatinous.	Some frostiness; an occasional "fairy ring."[a]	A little purple on blue field.	All in moss-like forms.

NO. 1983. PASTEURIZED BUTTER (THAT IS, MADE FROM PASTEURIZED CREAM).

Observer.	Light field.	Dark field.	Polarized light, crossed nicols.	Polarized light, with selenite plate.	Melted on slide at 60°-70° C. Appearance of curd.
F. D. Simons	Fairly smooth; abundant casein spots, pale yellow, dry.	Casein gelatinous.	Very slight haziness.		Fleecy or moss-like straggling forms.
G. E. Patrick	Smooth; no casein spots.	Nothing	Nothing	Nothing, or very faint purple on blue field.	Imperfect moss-like forms; less cohesion than in unpasteurized butter.

NO. 1984. RENOVATED BUTTER.

Observer.	Light field.	Dark field.	Polarized light, crossed nicols.	Polarized light, with selenite plate.	Melted on slide at 60°-70° C. Appearance of curd.
F. D. Simons	Rough; casein spots very abundant, pale yellow, inclosed in brine drops.	Casein gelatinous.	Frosty		Coarse particles of curd, mostly inclosed.
G. E. Patrick	Rough, many large casein spots, pale yellow, mostly dry.	Many large casein spots, gelatinous.	Some haziness; rarely a perfect or imperfect butter-fat rosette.	Some faint purple on blue. The fat rosettes are red and green on blue.	Much curd in coarse particles; some in fine particles. No moss-like or straggling forms; no cohesion.

[a] "Fairy rings" is the name given in the writer's laboratory notebooks to the very minute circles frequently seen in butters when viewed by polarized light with nicols crossed, and often seen to be made up of four quarter-circles (or arcs of 90° each). They are apparently the peripheries of minute butter-fat rosettes, the rosettes themselves not being visible, perhaps never having taken form.

The results of the two workers by microscopic examination agree in all particulars of importance, the principal differences being in regard to the "casein spots" of genuine butters viewed in the light and dark fields, one observer being able to see them much better than the other. They agree perfectly in differentiating sharply between the renovated and the genuine butter, and in showing the usefulness of the new mode of observation proposed by the writer, namely, as to the appearance of the curd when the mounts are melted on the slide. The pasteurized butter did not yield results sufficiently characteristic to distinguish it with any certainty from the other genuine butters. None of the "glistening" casein spots noticed in one of last year's pasteurized butters, when viewed in the dark field, were seen in this year's sample. The only peculiarity observed, and this by only one observer, was in the appearance of the curd when the mounts were melted on the slide—it was less cohesive than is usual in unpasteurized genuine butters and consequently showed only imperfect moss-like forms. This difference has long been observed by the referee and was recorded by him in the results of last year's work. Sometimes the moss-like forms will be entirely absent from the curd of a pasteurized butter, sometimes they will be merely imperfect, as in the sample studied this year. But this appearance is found not to be confined to pasteurized butters, as it is exhibited also by (saltless?) sweet-cream butters, and even by some regular creamery butters when old; therefore, it is by no means a distinguishing test, and we must admit that we have none for the certain identification of pasteurized butter.

THE WATERHOUSE TEST, MODIFIED.

In Circular No. 19, revised, it was suggested that the collaborators in this work should make comparative trials of very rapid and very gentle stirring while the butter is melting in the water at just below 50° C. before the stirring in the actual test is begun. From previous observations it was thought that different results might ensue. But none of the workers seems to have made this comparison except the referee, whose results in Tables VIII, IX, and X are marked respectively (b) and (c), for the very rapid and the very slow stirring (during melting), and (a) for the "gentle" stirring called for in the regular directions of the test.

The results on the creamery and dairy butters are shown in Table VIII.

TABLE VIII.—*The Waterhouse test, modified.*

NO. 1981. CREAMERY BUTTER.

Observer.	Result.	Final temperature.		Appearance when melted before stirring.
		In pan.	In cup.	
		°*C.*	°*C.*	
Mr. Kenney	Granulated	17.0	17.0	Granular.
Mr. Simons	do	....	14.0	Do.
Messrs. Woll and Olson	do	15.0	18.5	Oily.
Mr. Patrick:				
(*a*) Stirred "gently" during melting.	do	16.3	16.5	Not oily; a few small oil drops.
(*b*) Stirred very rapidly during melting.	do	17.5	17.7	Not oily at all.
(*c*) Stirred very slowly during melting.	Gathered; soft flat mass, 8 minutes; soft lump, 9 minutes.	....	....	Many small oil drops.
NO. 1982. DAIRY BUTTER.				
		°*C.*	°*C.*	
Mr. Kenney	Granulated	16.0	16.0	Granular.
Mr. Simons	do	....	14.0	Granular, with a few oil globules.
Messrs. Woll and Olson	do	15.5	18.5	Oily.
Mr. Patrick:				
(*a*) Stirred "gently" during melting.	do	14.0 (?)	14.5 (?)	Not oily; some small oil drops.
(*a*) Stirred "gently" during melting.	do	18.0	18.5	Do.
(*b*) Stirred very rapidly during melting.	do	16.5	16.5	Not oily at all.
(*b*) Stirred very rapidly during melting.	do	17.5	17.5	Do.
(*c*) Stirred very slowly during melting.	do	16.5	16.7	Some oil drops.
(*c*) Stirred very slowly during melting.	do	17.0	17.3	Many oil drops.

The results in Table VIII agree perfectly among themselves on the main result, when the regular method was employed, and disagree only on the "appearance when melted," an observation that has always been unsatisfactory because the result is frequently indefinite and is always more or less dependent upon the rapidity of the stirring during melting. Very rapid stirring during melting (b) of course did not change the main result with either of these butters, but did render them both "not at all oily" in the observation just mentioned; whereas very slow stirring during melting (c) not only increased the oiliness but even caused the creamery butter to gather at the end of eight minutes.

The results on the pasteurized butter are given in Table IX.

Table IX.—*The Waterhouse test, modified*—Continued.

NO. 1983. PASTEURIZED BUTTER.

Observer.	Result.	Final temperature.		Appearance when melted, before stirring.
		In pan.	In cup.	
		°*C.*	°*C.*	
Mr. Kenney	Granulated	16.0	16.0	Granular.
Mr. Simons	do		14.0	Semigranular, with few oil globules.
Messrs. Woll and Olson	Gathered; soft, flat mass, 7 minutes; soft lump, 8 minutes.	15.0	18.0	Oily.
Mr. Patrick:				
(a) Stirring "gently" during melting.	Granulated	16.7	16.7	Not oily, but many small oil drops.
(b) Stirring very rapidly during melting (Nov. 16).	do	16.7	16.7	Not oily.
(b) Stirring very rapidly during melting (Nov. 16).	do			Do.
(c) Stirred very slowly during melting (Nov. 16).	Gathered; soft, flat mass, 7 minutes; soft lump, 8 minutes.	16.5	16.5	Do.
(c) Stirred very slowly during melting (Nov. 16).	do	17.0	17.0	Not oily, but some small oil globules.
(b) Stirred very rapidly during melting (Dec. 1).	Gathered; no soft, flat mass; soft lump, 9½ minutes.	16.5	16.5	Not oily.
(b) Stirred very rapidly during melting (Dec. 1).	Gathered; no soft, flat mass; soft lump, 10 minutes.	16.5	16.5	Do.
(c) Stirred very slowly during melting (Dec. 1).	Gathered; soft, flat mass, 8 minutes; soft lump, 8½ minutes.			Oily; many oil drops.
(b) Stirred very rapidly during melting[a] (Dec. 8).	Granulated	18.0	18.0	
(c) Stirred very slowly during melting[a] (Dec. 8).	do	16.0	16.0	Do.

[a] Portion from interior of print.

By the regular method the pasteurized butter showed only one disagreement. In the hands of Messrs. Woll and Olson the butter gathered to a soft flat mass in 7 minutes, to a soft lump in 8 minutes, figures, however, which entirely preclude the possibility of its being mistaken for a renovated butter. The fact that in the work of Messrs. Woll and Olson the final temperatures in the pan and the cup were always several degrees apart shows that they worked in a slightly different way from that prescribed, probably, as last year, using a glass beaker instead of a tin cup. But the variation in method, whatever it was, did no harm, for no wrong conclusion was in any case reached. The result merely revealed a tendency to gather on the part of this butter, a tendency always exhibited in greater or less degree by pasteurized butters. And it must not be forgotten that certain other butters, perhaps sweet cream butters as a class, and without doubt occasional samples of genuine dairy butter, exhibit the same tendency. But their time records and appearance in the test distinguishes them from renovated butter.

The tests by the referee, comparing very rapid (b) and very slow (c) stirring during melting, are also recorded in Table IX; they show that sometimes the slow stirring (c) apparently caused the butter to gather and that sometimes the very rapid stirring (b) did not suffice to prevent its gathering. The tests on December 8 indicate that exposure to air, that is, oxidation, rancidity, and age, may have something to do with the behavior.

The results on the renovated butter, No. 1984, are exhibited in Table X.

TABLE X.—*The Waterhouse test, modified—Concluded.*

NO. 1984. RENOVATED BUTTER.

Observer.	Result.	Final temperature.		Appearance when melted before stirring.
		In pan.	In cup.	
		°*C.*	°*C.*	
Mr. Kenney	Gathered	17.0	17.0	Oily.
Mr. Simons	Gathered; soft flat mass, 4 minutes; soft lump, 8 minutes.	....	14.0	Do.
Messrs. Woll and Olson	Gathered; soft flat mass, 4 minutes; soft lump, 6 minutes.	14.0	17.5	Not oily.
Mr. Patrick:				
(a) Stirred "gently" during melting.	Gathered; soft flat mass, 5 minutes; soft lump, 9 minutes.	16.0	16.0	Oily; many oil drops. More oily after stirring 2 minutes.
(b) Stirred very rapidly during melting.	Gathered; soft flat mass, 4 minutes; soft lump, 9 minutes.	16.5	16.5	Not oily; some oil drops More oily after stirring 2 minutes.
(b) Stirred very rapidly during melting (Dec. 2–6).	Gathered; soft flat mass, 4½ minutes; soft lump, 8 minutes.	16.5	17.0	Do.
(b) Stirred very rapidly during melting (Dec. 2–6).	Gathered; soft flat mass, 4¼ minutes; soft lump, 9 minutes.	16.7	16.7	Do.
(c) Stirred very slowly during melting (Dec. 2–6).	Gathered; soft flat mass, 4 minutes; soft lump, 9½ minutes.	16.7	16.7	Oily; many oil drops.
(c) Stirred very slowly during melting (Dec. 2–6).	Gathered; soft flat mass, 4½ minutes; soft lump, 9 minutes.	16.2	16.5	Do.

In Table X the results on the renovated butter are in entire agreement as to the main result and almost entirely so as to the time record. The variation in method evidently practiced by Messrs. Woll and Olson probably showed its effect in the time record of their experiment, which is slightly different from all the others.

The trials of rapid and slow stirring during melting, (b) and (c) in the table, show no differences whatever except in the appearance after melting—that is, in regard to oiliness.

Remarks upon the results by the Waterhouse test.

The combined results of the work with the Waterhouse test this year show that less dependence is to be placed upon the appearance of the charge after melting, as to oiliness or non-oiliness, than was formerly thought, since this appearance depends to a large extent upon the speed of stirring during melting. It would seem advisable, in order to secure uniformity in this matter and also to prevent the gathering of butters that have only a slight tendency in that direction, to prescribe hereafter that the charge be stirred *rapidly* during melting, instead of gently, all other conditions remaining the same as heretofore.

REMARKS UPON THE WORK ON RENOVATED BUTTER AS A WHOLE.

The work above reported shows in general such close agreement, not only in regard to the main results, upon which the expert mainly depends in passing judgment upon a butter, but also in regard to most of the details of observation, that the referee sees no need for the further continuance of this work.

RECOMMENDATIONS.

It is recommended that the referee for next year be requested to continue the study of the effects of preservatives, especially formaldehyde and carbon bisulphid, upon the determination of the proteids of milk, and to take up the study (1) of the methods of determining sugars in condensed milks and dried milks or milk powders, and (2) of methods for detecting the adulteration of butter with small amounts of foreign fats, especially animal fats.

Mr. Yoder stated that he had examined some samples of milk before and after condensing and found that there had apparently been losses in fat. The question was asked whether any other chemist had had a similar experience or had any knowledge of the fat existing in such condition that it could not be extracted by ether according to the ordinary method.

Mr. Patrick replied that the difficulty of extracting fat from sweetened condensed milk by the usual method was quite well known. Geisler [a] having investigated the subject and found that very good results could be obtained by using only 1 gram of condensed milk with 3 or 4 grams of water, drying, and extracting for a very long time. Mr. Patrick further stated that in his opinion one of the methods in which the fat is set free by an acid is preferable to the ether extraction method for the analysis of condensed milk.

MILK ANALYSIS BY CALCULATION.

By G. A. OLSON.

The application of some short method for estimating the per cent of protein in milk has received the attention of a number of investigators. At the Wisconsin station some time has been spent in studying this problem but without any satisfactory results having been reached. The methods which have been devised always call for careful and more or less complicated manipulations, so that the methods, although promising, have, on the whole, not as yet been brought to a successful issue.

In looking over the literature on this subject we find in the Analyst (vol. 25, p. 170), the following formula computed by Richmond for the calculation of the proteids of milk:

$$P = 2.8T + 2.5A - 3.33F - 0.7\frac{G}{D},$$

when P=proteids, T=total solids, A=ash, D=specific gravity, and G=excess density ($1{,}000D - 1{,}000$), or the lactometer reading. This formula is based upon the following specific gravities of the constituents of milk: Milk sugar=1.667, protein=1.346, fat=0.93, and ash=4.12.

Richmond deduced the above formula from these specific gravities and the average composition of milk. The writer has been unable to obtain results of any marked degree of accuracy by applying this formula to different analyses of milk. If, on the other hand, the formula is empirically changed as given below, the calculated results will agree rather closely with those obtained by chemical analysis.

$$P = \frac{2.8T + 2.5A - 3.33F}{7.2}; \text{ or}$$

$$P = .39T + .347A - .462F.$$

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[a] J. Amer. Chem. Soc., 1900, *22:* 637.

In order to reach, if possible, more correct results by the calculated method, the writer made calculations of the various factors and arrived at the following formula:

$$P=\frac{2.32T+2.07A-2.41F}{6.3}\text{; or}$$

$$P=.368T+.33A-.383F.$$

This formula has been used exclusively in the calculations submitted in this paper by the writer.

Applying Richmond's formula for total solids,

$$T=\tfrac{1}{4}L+1.2F+0.14,$$

or Babcock's formula,

$$T=\frac{L}{4}+1.2F,$$

and asssuming that all milk contains a definite amount of ash, viz, 0.75 per cent, a complete analysis can, therefore, be computed by this method by determining only the specific gravity and the per cent of fat of the milk in question, the sugar being obtained by difference.

Gravimetric determinations were made of seven different samples of milk and the specific gravities determined in each case. In sample No. 2 the fat content was determined by the Babcock test. Sample No. 4 was taken from three-quarters of the cow's udder and No. 5 from the remaining quarter. The other five samples were morning milkings from a single herd taken at intervals of two weeks.

Table I.—*Comparison of determined and calculated milk analyses.*

Method.	Sample No.	Specific gravity.	Solids.	Protein.	Fat.	Sugar.	Ash.
			Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Gravimetric	1	1.0304	12.86	**2.98**	4.41	4.70	0.69
Calculated			12.88	**3.30**	4.40	4.43	.75
Gravimetric	2	1.0303	13.04	**3.31**	4.35	4.66	.72
Calculated			12.97	**3.36**	4.35	4.51	.75
Gravimetric	3	1.0320	13.24	**3.44**	4.22	4.64	.76
Calculated			13.28	**3.45**	4.4	4.68	.75
Gravimetric	4	1.0340	11.97	**3.69**	2.87	4.68	.73
Calculated			12.10	**3.56**	3.00	4.79	.75
Gravimetric	5	1.0346	11.28	**3.81**	2.14	4.52	.81
Calculated			11.35	**3.57**	2.25	4.78	.75
Gravimetric	6	1.033	13.22	**3.38**	4.14	4.95	.75
Calculated			13.35	**3.54**	4.25	4.81	.75
Gravimetric	7	1.033	13.43	**3.52**	4.30	4.89	.72
Calculated			13.53	**3.55**	4.40	4.83	.75
Gravimetric	[a] 8	1.0325	12.72	**3.45**	3.78	4.75	.74
Calculated			12.78	**3.48**	3.86	4.69	.75

[a] Average of the seven analyses.

Table I shows a remarkable agreement, the differences being within the limits of unavoidable analytical errors for all the different constituents of the milk.

The preceding formula was used for the calculation of protein in a large number of complete analyses of milk in the literature on dairying, with the results shown in Table II. Mr. F. W. Woll gave 92 complete analyses of composite samples of the milk from pure-bred cows in the Wisconsin Annual Report, 1901, pages 87–90. A summary of the analytical data, compared with the calculated results, is as follows:

Table II.—*Comparison of average and extremes of 92 analyses (Woll) with calculated results.*

Average and limits.	Method.	Specific gravity.	Solids.	Protein.	Fat.	Sugar.	Ash.
			Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Average	Gravimetric	1.0312	12.20	**3.24**	3.63	4.57	0.76
	Calculated		12.09	**3.22**	3.63	4.49	.75
Maxima	Gravimetric			**4.12**		5.20	.92
	Calculated			**3.80**		5.13	.75
Minima	Gravimetric			**2.47**		3.63	.62
	Calculated			**3.01**		3.78	.75

Richmond reported 50 complete analyses of milk in the Analyst, on which the following comparison is based:

TABLE III.—*Comparison of average and extremes of 50 analyses (Richmond)* [a] *with calculated results.*

Average and limits.	Method.	Specific gravity.	Solids.	Protein.	Fat.	Sugar.	Ash.
			Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Average	Gravimetric	1.032	12.49	3.42	3.71	4.62	0.74
	Calculated		12.61	3.47	3.71	4.68	.75
Maxima	Gravimetric			3.76		4.96	.82
	Calculated			3.55		4.72	.75
Minima	Gravimetric			3.19		3.65	.67
	Calculated			3.45		4.16	.75

[a] 1899, *24:* 198–199.

In the New Jersey Report for 1880 (p. 59) 38 complete analyses of Jersey, native, and Ayrshire cows are reported, which are used in Table IV:

TABLE IV.—*Comparison of average and extremes of 38 analyses (New Jersey) with calculated results.*

Average and limits.	Method.	Specific gravity.	Solids.	Protein.	Fat.	Sugar.	Ash.
			Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Average	Gravimetric	1.0324	13.73	3.41	4.69	4.78	0.85
	Calculated		13.84	3.55	4.69	4.85	.75
Maxima	Gravimetric			3.79		5.12	1.07
	Calculated			3.61		4.91	.75
Minama	Gravimetric			3.04		4.50	.56
	Calculated			3.40		4.57	.75

Tables V, VI, VII, and VIII have been arranged on the same basis.

TABLE V.—*Comparison of average and extremes of 11 analyses (Fleischmann* [a]*) with calculated results.*

Average and limits.	Method.	Specific gravity.	Solids.	Protein.	Fat.	Sugar.	Ash.
			Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Average	Gravimetric	1.0319	12.15	3.42	3.48	4.53	0.72
	Calculated		12.30	3.45	3.48	4.62	.75
Maxima	Gravimetric			3.91		4.91	.76
	Calculated			3.52		4.71	.75
Minima	Gravimetric			3.21		3.94	.67
	Calculated			3.50		4.51	.75

[a] Landw. Versuchs-Stat., 1879, p. 24; Milchw. Versuchs-Stat., Raden, 1884.

TABLE VI.—*Comparison of average and extremes of 4 analyses (Connecticut* [a]*) with calculated results.*

Average and limits.	Method.	Specific gravity.	Solids.	Protein.	Fat.	Sugar.	Ash.
			Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Average	Gravimetric	1.0323	13.49	3.48	4.23	5.02	0.72
	Calculated		13.29	3.53	4.23	4.83	.75
Maxima	Gravimetric			3.56		5.20	.83
	Calculated			3.55		4.86	.75
Minima	Gravimetric			3.37		4.86	.62
	Calculated			3.45		4.85	.75

[a] Agr. Exper. Stat. Rept., 1897, p. 322

Table VII.—*Comparison of average and extremes of 5 analyses (Dircks [a]) with calculated results.*

Average and limits.	Method.	Specific gravity.	Solids.	Protein.	Fat.	Sugar.	Ash.
			Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Average	Gravimetric	1.0325	12.48	**3.16**	3.87	4.74	0.71
	Calculated		12.77	**3.42**	3.87	4.75	.75
Maxima	Gravimetric			**3.31**		4.72	.73
	Calculated			**3.33**		4.76	.75
Minima	Gravimetric			**3.04**		4.61	.70
	Calculated			**3.41**		4.56	.75

[a] Milchztg., 1887, *16:* 85.

Table VIII.—*Comparison of average of 705 analyses (König [a]) with calculated results.*

Method.	Specific gravity.	Solids.	Protein.	Fat.	Sugar.	Ash.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Gravimetric	1.0313	12.73	**3.39**	3.68	4.94	0.72
Calculated		12.37	**3.39**	3.68	4.55	.75

[a] Chemie der menschlichen Nahrungs- und Genussmittel, *2:* 602.

It will be noted that the calculated figures for protein are approximately the same as those in the actual analyses given. So far as the writer has been able to ascertain, this formula will hold good in the case of all normal milks. If this conclusion is correct it can, therefore, be recommended for use in all cases where it is desired to determine the percentages of the various constituents found in the milk without actually making determinations of the milk proteids. In the same way that tables have been constructed for solids not fat, for given percentages of fat and specific gravities, it would be feasible to arrange tables by which the per cent of proteids in samples of milk corresponding to certain contents of fat and specific gravities might be ascertained at a glance.

FRIDAY—AFTERNOON SESSION.

REPORT ON SOILS.

By Cyril G. Hopkins, *Referee.*

Some work has been done by Messrs. Peter and Averitt, of the Kentucky station, on the "Proper strength of acid for soil digestion," on which a paper will be read by Mr. Averitt. This is a continuation of the work by Mr. Peter with fifth-normal nitric acid for the determination of available plant food in soils, which was reported through the referee last year and recommended for further investigation.

Recommendations.

It is recommended—

(1) That the determination of water-soluble plant food contained in the soil be further investigated.

(2) That further study be made of the use of fifth-normal nitric acid in the determination of available plant food.

(3) That the use of ammonium sulphate for the removal of the last appreciable amount of barium from the solution of total alkalies be thoroughly tested with a view to its incorporation in the official methods.

(4) That the sodium peroxid method for ultimate analysis and the preliminary separation of phosphorus as iron phosphate in ammoniacal solution previous to its resolution and precipitation as ammonium phospho-molybdate be investigated.

In connection with this report the referee desires to present the following paper on the results of a pot-culture experiment on the comparative value of steamed bone meal and finely ground raw rock phosphate, which furnishes some information regarding the comparative availability of the insoluble phosphorus of natural rock phosphate and may have some bearing upon the methods of analysis and the proper valuation of that material.

COMPARATIVE VALUE OF STEAMED BONE MEAL AND FINELY GROUND NATURAL ROCK PHOSPHATE.

By Cyril G. Hopkins.

Steamed bone meal and raw rock phosphate may be called natural products. A good grade of either of these materials contains about 12½ per cent of the element phosphorus, or nearly 30 per cent of so-called "phosphoric acid." These natural products have absolutely no injurious effect on the land, either immediate or subsequent. They may be safely applied in almost any amount, and they will remain in the soil until removed by cropping.

The fact that steamed bone meal costs $25 to $30 a ton, while finely ground natural rock phosphate, equally rich in phosphorus, can be bought for one-third as much, has led several experiment stations to investigate the practicability of using raw rock phosphate. Some of the most practical trials have been made in Ohio, Maryland, and Illinois, and the results obtained are reported in the literature from those experiment stations.

A series of pot-culture experiments recently conducted at the Illinois station furnishes some additional data on the relative values of steamed bone meal and raw rock phosphate. The soil used was from the gray silt loam prairie of the Lower Illinois glaciation, a soil which is distinctly acid. Wheat was the crop grown in the pots.

The phosphate used is known as the "blue rock phosphate," which is thought to be somewhat more readily available than the "brown rock phosphate," the former being an unweathered, bedded phosphate, and the latter a leached, phosphatic limestone. In certain pots the phosphorous fertilizer was turned under with a catch crop of clover, in other pots with farm manure, and in others with both clover and manure. In all cases equal money values of bone meal and rock phosphate were applied; that is, the quantity of rock phosphate applied was three times the application of bone meal.

The following tabular statement shows the results obtained:

Table I.—*Comparative effect of steamed bone meal and raw rock phosphate in connection with clover and manure.*

POTASSIUM NOT ADDED.

Soil pot No.	Treatment applied.	Wheat yields.		Increase bushels per acre.
		Grams per pot.	Bushels per acre.[a]	
101	None	10.0	27	....
102	Clover	16.3	43	16
103	Bone meal	14.7	39	12
104	Rock phosphate	14.2	38	11
105	Clover, bone meal	22.2	59	32
106	Clover, rock phosphate	23.3	62	35
107	Manure	16.5	44	17
108	Clover, manure	22.7	60	33
109	Manure, bone meal	19.4	52	25
110	Manure, rock phosphate	19.5	52	25
111	Clover, manure, bone meal	23.1	62	35
112	Clover, manure, rock phosphate	23.3	62	35

[a] The pots used in these investigations are 10½ inches in diameter; consequently 1 gram per pot corresponds to 1 pound per square rod, or to 160 pounds per acre.

Table I.—*Comparative effect of steamed bone meal and raw rock phosphate in connection with clover and manure*—Continued.

POTASSIUM ADDED.

Soil pot No.	Treatment applied.	Wheat yields.		Increase bushels per acre.
		Grams per pot.	Bushels per acre.	
113	Potassium	11.3	30	3
114	Clover, potassium	18.4	49	22
115	Potassium, bone meal	18.4	49	22
116	Potassium, rock phosphate	18.2	49	22
117	Clover, potassium, bone meal	21.9	58	31
118	Clover, potassium, rock phosphate	21.9	58	31
119	Manure, potassium	18.1	48	21
120	Clover, manure, potassium	19.1	51	24
121	Manure, potassium, bone meal	19.3	51	24
122	Manure, potassium, rock phosphate	19.0	51	24
123	Clover, manure, potassium, bone meal	25.3	67	40
124	Clover, manure, potassium, rock phosphate	25.3	67	40
125	None	10.6	28	....

It will be seen that the untreated soil (pot No. 101) yielded at the rate of 27 bushels of wheat per acre (28 bushels on the duplicate pot, No. 125). Where clover had been turned under (No. 102) the yield was increased by 16 bushels—that is, from 27 to 43—and where bone meal was turned under with clover (No. 105) the rate of yield was 59 bushels per acre, the increase of 32 bushels being just double that produced by clover without bone meal.

Where raw rock phosphate was turned under with clover (No. 106) the wheat yielded at the rate of 62 bushels per acre, making a total increase of 35 bushels over the yield of the untreated soil. Of this 35-bushel increase, 16 bushels should be credited to the clover, 11 bushels to the phosphate, and 8 bushels evidently to the power of the decaying clover residues to liberate additional phosphorus from the rock phosphate. Thus it will be observed that rock phosphate used alone produced an increase of only 11 bushels, which, added to the increase of 16 bushels due to clover alone, makes only 27 bushels increase. In other words, the sum of the gains which they make when used separately was 8 bushels less than the increase produced when the rock phosphate and clover were turned under together.

Somewhat similar results are produced with clover and bone meal when used separately and together, also with bone meal and potassium and with rock phosphate and potassium, one of the chief functions of the potassium apparently being to increase the availability of the phosphorus in the bone meal and in the rock phosphate. Such extraordinary combined action does not appear, however, from other combinations.

As a general average, the rock phosphate has made slightly better gains than the steamed bone meal.

A MODIFIED METHOD FOR THE DETERMINATION OF TOTAL PHOSPHORUS IN SOILS.

By J. H. Pettit and A. Ystgard.

Though sodium peroxid has been used in some instances as an agent for breaking down refractory compounds in rock and mineral analysis, no mention has been found by the authors in the literature of the subject of its use in ultimate soil analysis. The great advantage in using sodium peroxid is the rapidity of the process. There is a further advantage in the case of soils, in that there always exists an oxidizing condition. On the other hand, in the alkali carbonate fusion of a soil with considerable organic matter, a reducing condition may exist which would result in the loss of elements like phosphorus.

The manipulation used for the determination of phosphorus alone is as follows:

Weigh out 15 grams of sodium peroxid in an iron crucible or dish, transfer about 3 grams to a watch glass, and mix thoroughly 5 grams of soil with the peroxid remaining in the crucible. Cover the mixture with the 3 grams of peroxid. Heat the mixture carefully, applying the flame of a Bunsen burner directly upon the surface of the charge, until the action begins. Cover the crucible until the reaction is over, and keep at a low red heat for fifteen minutes; do not allow melting to take place. By means of a large funnel and a stream of cold water, transfer the charge to a 500 cc measuring flask; acidify with hydrochloric acid and boil for five minutes; allow to cool and make up to the mark. If the action has taken place properly there will be no particles of undecomposed soil in the bottom of the flask. Allow the silica to settle and draw off 200 cc. of the clear solution. Evaporate to dryness and bake in an air bath for five hours at 110°. Take up with hydrochloric acid, heating if necessary, and filter out the silica.

Precipitate the iron, aluminum, and phosphorus by adding ammonium hydroxid; filter, wash, and dissolve the precipitate on the filter with warm hydrochloric acid. Run the filtrate and washings to dryness and bake again. Take up with hydrochloric acid, heating if necessary, filter out any silica and evaporate the filtrate and washings to about 10 cc. Add 2 cc of concentrated nitric acid and just neutralize with ammonium hydroxid. Clear up with nitric acid, avoiding an excess. Heat to 50° to 60° on the water-bath, add 15 cc of molybdic solution, keeping at this temperature two hours. Allow to stand over night, filter and wash with a one-tenth per cent solution of ammonium nitrate until free of acid, and finally wash twice with water. Transfer the hydroxid filter to a beaker, dissolve in standard potassium hydroxid, and titrate the excess of potassium with standard nitric acid, using phenolphthalein as indicator. For strength of solution see page 13, Bulletin 46, U. S. Department of Agriculture, Division of Chemistry.

To make a complete ultimate analysis, the hydrochloric acid solution of the mass resulting from the reaction is first run to dryness, baked, and the silica filtered out. This filtrate is again run to dryness and baked to throw out practically all of the remaining silica. Some small amount will still remain, however, and for the volumetric phosphorus determinations the aliquot is first precipitated with ammonium hydroxid and the phosphorus determined after redissolving the precipitate in hydrochloric acid.

Comparing the peroxid method with the alkali carbonate method the following results were obtained when the same method for freeing the solution of silica is used in the carbonate method as given for the peroxid method:

Table I.—*Comparison of the carbonate and peroxid methods for the determination of phosphorus.*

[Dry basis.]

Soil No.	Carbonate method.	Peroxid method.
	Per cent.	*Per cent.*
1544	0.086	0.086
1550	.129	.132
1553	.140	.149
1562	.218	.222

A sample of blue rock phosphate analyzed by the usual aqua regia digestion method showed 13.18 per cent phosphorus. By the sodium peroxid method it showed 13.25 per cent phosphorus. When mixed with pure silica and determined by the peroxid method it showed 13.29 per cent phosphorus.

A definite amount of the rock phosphate was added to soils which had been analyzed for phosphorus and the following results were obtained. The calculated results were obtained from the separate analysis of the rock and soil:

Table II.—*Comparison of calculated and determined results on phosphorus in soils.*

Soil No.	Determined.	Calculated.
	Per cent.	*Per cent.*
1571	0.320	0.317
1573	.294	.298

To subsoils which are low in organic matter it is necessary to add 0.5 gram of starch to start the reaction. Ten decompositions can be made in two and one-half hours by this method.

The following table gives some duplicate determinations of total phosphorus as obtained in our ordinary laboratory work by this method:

TABLE III.—*Duplicate determinations of phosphorus by suggested method.*

Soil No.	Phosphorus.		Soil No.	Phosphorus.	
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
1541	0.046	0.046	1559	0.057	0.061
1542	.038	.038	1560	.050	.050
1543	.059	.058	1561	.044	.045
1547	.062	.065	1562	.094	.097
1548	.048	.048	1563	.074	.074
1549	.047	.043	1564	.065	.065

Mr. W. H. **Bowker**, Boston. I want to thank you for your courtesy in stopping your proceedings to allow me to speak for a moment concerning fertilizer legislation.

As to a National law, I can only speak for myself; I am not authorized to speak for the manufacturers. Personally I should favor a National law that requires a uniform statement of analysis in all the States, as it would simplify interstate traffic. Whether such a measure should go further than providing for a uniform statement is a very grave question.

In 1873 I had the pleasure of taking a very active part in getting an inspection law passed in Massachusetts, which became the basis of nearly all similar legislation in other States. I contended then that it would help the business by giving it a legitimate standing; and it did, as we all know. I think the principle, to state what you sell and sell what you state, should prevail in every line of business—the food products which I buy or the plant food which I sell. Neither do I believe that one class of merchants or manufacturers should be singled out in this requirement and another class go free. At the same time the fertilizer manufacturers are not objecting, because they believe it has helped their business; and I do not think there is an honorable manufacturer of fertilizers to-day who would have the fertilizer inspection laws of this country repealed.

Now, as these State laws have been good for all concerned a uniform National law may be better; but I suggest that the first thing to be done is that you agree among yourselves as to what that law shall be. Let me suggest also that you make it as liberal as you can for those who are to work under it, remembering that you are bound to protect the interests of both the seller and the buyer, for both are citizens and taxpayers. When you have agreed among yourselves then bring it to us and we will have a joint conference, and that, I understand, is the course you propose to follow. If it seems best to have these State laws superseded by a National law, I feel very confident that the manufacturers will not object, provided it is a reasonable one and they are given a chance to consider it with you before it is enacted.

May I say a word on the methods of analysis, more particularly the method which relates to the determination of potash? I think it should be modified; and I am not going to appeal to you on the ground that it will help us solely, for I think it will help the consumer also. Your method of determining potash, I believe, does not find all the potash that is present in mixed fertilizers or raw materials, especially if it is present in organic forms. Now, since the inspection laws were passed which called for water-soluble potash there has been a great revolution in all industrial affairs, and, as you know, a great many by-products have come in which were never dreamed of as sources of plant food. The great by-product of cottonseed meal has been introduced as a commercial source of plant food since the Massachusetts law was passed. We are now getting organic forms of potash from many sources and many countries, particularly beet-sugar refuse, which also contains nitrogen. We can probably bring in thousands of tons of it, and it is a valuable source of plant food, but we have to pay for every unit of nitrogen and every unit of potash which it contains, and if we can not get credit in your analyses for all the potash which it carries we can not afford to buy it. If, however, we do get credit we shall bring in such materials, and it will help to keep down the cost of all manurial substances and, of course, the cost of mixed goods.

One word more occurs to me in relation to a National law. If it is decided to ask for such a law, and it goes further than a uniform statement, I urge that provision be made for adequate and fair sampling; further, that provision be made for deficiencies and excesses. In our Massachusetts law there can be no prosecution if the goods are substantially equivalent to the guarantee. For example: If there is a deficit of, say, one-fourth of 1 per cent in nitrogen and an excess of phosphoric acid and potash which more than counterbalances the deficiency in nitrogen, it is plain that there has been no intent of fraud and therefore there can be no prosecution. It is impossible for us to manufacture absolutely to the line, but if our goods are substantially equivalent then it seems to me we have done all that we should be expected to do, assuming, of course, that our goods are not out of balance. This custom prevails in the trade between manufacturers, and it should prevail when selling to consumers.

Gentlemen, I again want to thank you for your courtesy in listening to me, and assure you that if the matter of a National law comes up I sincerely believe the manufacturers will be glad to meet you in joint conference, and that you will find them entirely reasonable in their views.

ON THE PROPER STRENGTH OF ACID TO BE USED FOR DETERMINING AVAILABLE PLANT FOOD IN SOILS.

By ALFRED M. PETER and S. D. AVERITT.

The results presented last year in the report of the referee on soils agree in showing that neither water nor N/200 hydrochloric acid under the conditions there described possesses solvent power for the phosphorous compounds strong enough to give any idea of the amount of available phosphorus in the soils tested. The agricultural significance of amounts of phosphorus ranging from two to eight parts to the million of soil is almost infinitesimal. And when we compare the amounts obtained from referee's samples Nos. 1 and 2 we find a difference in favor of the rich soil of only about one pound in the million, as shown by solution in N/200 hydrochloric acid, or not exceeding 5.4 parts, as shown by the water solution, making it very apparent that these figures stand in no definite relation to the values which we are trying to measure. The case is much better with potassium. The Rothamstead soil (B3A) which had received potassium salts yielded to N/200 hydrochloric acid 112.6 parts of that element per million more than the soil that received no potassium and to water 42.4 parts more, or the equivalent of about 170 and 64 pounds per acre, respectively, in the first 6 inches, amounts within the comprehension of the practical agriculturist and sufficient to account for a marked difference in fertility. But the differences between the referee's rich soil No. 1 and poorer soil No. 2, are much less, averaging 15 parts per million for N/200 hydrochloric acid and 11.6 for water. It was shown, however, that the action of a somewhat stronger solvent brings out much greater differences between these two samples.[a] By digestion in N/5 nitric acid as used at the Kentucky station, sample No. 1, the richer soil, yielded 56 parts of phosphorus and 144 parts of potassium per million more than the poorer soil No. 2. These differences are more consistent with the known agricultural differences of the two soils in question than are those brought out by the weaker solvents.

In order to compare with these results the action on the two samples of acids of other dilutions between fifth normal and two hundredth normal, we have made determinations with N/10, N/20, and N/40 nitric acid and present the results in the following table, along with those obtained a year ago, with N/5 nitric acid and N/200 hydrochloric acid for comparison:

TABLE I.—*Comparison of results obtained with solvents of varying strength.*

[Parts in 1,000,000 of the moisture-free soil.]

AVAILABLE POTASSIUM.

Solvent.	N/5 nitric acid.	N/10 nitric acid.	N/20 nitric acid.	N/40 nitric acid.	N/200 hydrochloric acid.	Water.
Referee's sample No. 1	222	210	198	161	38.3	29.1
No. 2	90	108	76	69	29.4	17.4
Difference	132	102	122	92	8.9	11.7

AVAILABLE PHOSPHORUS.

Solvent.	N/5 nitric acid.	N/10 nitric acid.	N/20 nitric acid.	N/40 nitric acid.	N/200 hydrochloric acid.	Water.
Referee's sample No. 1	64	60	55	27	2.1	0.9
No. 2	11	9	6	5	Trace.	Trace.
Difference	53	51	49	22	2.1	0.9

In making the digestions allowance was made for the neutralizing power of the soils by adding an extra amount of acid determined by a preliminary digestion with N/5 nitric acid, but, through a mistake, only about half the proper amount was added in the digestion of No. 1 with N/40 acid. This may account for the apparent sudden falling off in this case, especially of the phosphorus. There is also an irregularity in the potash determination No. 2. Unfortunately the amount of material at hand was not enough to permit of a repetition of the determinations. The differences shown between the two samples appear to grow less as the strength of the acid solution diminishes, though not in proportion, and the preference still remains with the fifth normal strength.

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 90, p. 178.

A similar experiment was made with N/10 nitric acid upon samples of a rich bluegrass soil which had been analyzed about a year ago with N/5 nitric acid. The practical application in this case is very interesting. The 15-acre field from which the sample was taken in the fall of 1904 had been in tobacco that year, but on about 4 or 5 acres of it the crop was a failure for no apparent reason, whereas the rest produced a good crop. For the last ten years this field had been cultivated in a three-year rotation of tobacco, wheat, and clover, except that at the beginning of the series, ten years ago, the greater part was sown in hemp and only the 4 or 5 acre piece where the tobacco failed in 1904 was then planted with tobacco. Average samples were taken from adjacent parts of the good and bad tobacco areas.

Table II.—*Available potassium and phosphorus determined on soils producing successful and unsuccessful crops.*

[Parts in 1,000,000 of moisture-free soil.]

AVAILABLE POTASSIUM.

	Digestion in N/5 nitric acid.			Digestion in N/10 nitric acid.		
	1st 6″.	2d 6″.	2d 12″.	1st 6″.	2d 6″.	2d 12″.
Tobacco good in 1904	80	5	7	63	7	4
Tobacco failed in 1904	13	14	9	23	5	8
Difference	67	−9	−2	40	2	−4

AVAILABLE PHOSPHORUS.

	Digestion in N/5 nitric acid.			Digestion in N/10 nitric acid.		
	1st 6″.	2d 6″.	2d 12″.	1st 6″.	2d 6″.	2d 12″.
Tobacco good in 1904	2,424	3,035	3,341	2,070	2,593	3,275
Tobacco failed in 1904	3,392	3,545	3,486	3,162	3,257	3,371
Difference	−968	−510	−145	−1,092	−664	−96

In this case, also, the fifth normal acid brought out a greater difference in available potassium than did the tenth normal. The difference in solubility of the potassium compounds in top soil as compared with subsoil is also well brought out. The larger amount of potassium extracted from the soil of the good field is not caused by a larger total amount present, because a digestion in hydrochloric acid (sp. gr. 1.115) and analysis by the official methods gave 4,558 parts of potassium against 5,364 parts per million in the soil where the tobacco failed. The deficiency in available potassium is suggested as the cause of the failure of the crop.

The amount of available phosphorus in both these soils is so large as to render the differences shown of no practical significance, unless it be that they accentuate the unbalanced ratio between phosphorus and potassium.

THE PHOSPHORIC ACID REMOVED BY CROPS, BY DILUTE NITRIC ACID, AND BY AMMONIUM HYDROXID FROM A LIMED AND AN UNLIMED SOIL RECEIVING VARIOUS PHOSPHATES.

By B. L. Hartwell and J. W. Kellogg.

The material for this work was obtained from a field experiment at the Rhode Island station which has been conducted since 1894 to test the relative efficiency of different phosphatic materials upon unlimed and limed soils. All of the plots received the same treatment as regards potassium and nitrogen. One of the limed and one of the unlimed plots received no phosphorus, while the remaining plots received the same total amounts of phosphorus from the various sources in a series of applications ended in the spring of 1902. Since then no phosphorus has been added, although nitrogen and potassium were applied liberally each year.

Samples of the surface soil were collected in June of 1903 before the miscellaneous crops, which were planted across the plots in a few rows each, had made much growth. Samples of certain of these crops also were taken in the fall, so that a comparison might be made between the relative amounts of phosphoric acid removed from the soil by the plants and by extraction with certain solvents.

One ton of air-slaked lime per acre was added to half of the plots in 1894 and a second ton was applied on April 28, 1903. When the soil samples were taken, two months after the latter application of lime, there were small particles of the same which had become carbonated and had not been decomposed. It was found that these were not dissolved during the use of the lime-water method [a] for determining the acidity of soils, and it is evident, therefore, that with a recently limed soil the apparent acidity as determined by the lime-water method would be considerably less if all of the quite readily assimilable lime exerted its neutralizing effect during the operations of the method. It became evident also that comparative results could only be obtained by this method when the conditions of digestion were kept alike.

The details of this work, analytical results, etc., are reported in the Eighteenth Annual Report of the Rhode Island Agricultural Experiment Station for 1905.

Summary of Results.

The range in the percentages of phosphoric acid in oats, golden German millet, and Japanese barnyard grass, fertilized with different phosphates, was not wide enough to serve as a measure of the assimilability of the phosphorus from different materials. The results with flat turnips, however, indicate that this plant may serve a useful purpose in testing the relative assimilability of different phosphates.

The relative yields of turnip roots upon the limed phosphate plots, all of which had received equal amounts of phosphoric acid, ranged from 1.7 to 27.0, depending upon the kind of phosphate, as compared with the limed no-phosphate plot taken as 1.0. The percentage of phosphoric acid in the dry matter of the turnip roots varied between 0.45 and 0.87.

The general tendency was for the percentage of phosphoric acid in the turnip crop to increase with the increase in the size of the crop caused by the better kinds of phosphates.

It is possible that the percentage of phosphoric acid in the turnip may indicate the relative amounts of assimilable phosphoric acid in different soils when certain conditions are well understood.

Ammonium hydroxid of fifth normal, twenty-fifth normal, and one hundredth normal strength did not extract from the soil amounts of phosphorus in accord with the assimilability of the phosphorus in the different plots. Fifth normal and twenty-fifth normal nitric acid also failed to uniformly point out the differences in the assimilability of the phosphorus as shown by the crop results.

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[a] Veitch, J. Amer. Chem. Soc., 1902, *24:* 79.

The selection of an indicator for determining the neutralizing power which a soil exerts upon a dilute acid in which it is digested is of considerable importance in view of the widely different results secured by indicators of such unlike classes as methyl orange and phenolphthalein.

It is doubtful if any solvent will extract from all soils amounts of phosphorus bearing definite relations to those removed by even a given crop. This is especially true when a large portion of the total amount of this element is in combination with organic matter and must depend for its liberation, therefore, to a considerable extent, upon the microorganisms of the soil.

Mr. Moore, Mr. Huston, Mr. Hartwell, and Mr. Davidson discussed the soil papers at some length. Mr. Moore contended that the conclusion reached by Mr. Hopkins that no effect was produced by the addition of potash, and Mr. Averitt's statements as to the relations between crop yield and available plant food as shown by determinations with different solvents, could not be with certainty sustained, as all of the factors involved in the problem had not been considered. Pot experiments in which variation in climatic conditions was eliminated and the distribution of the elements of plant food throughout the crop was considered in connection with the availability of plant food in the soil (determined by a uniform method which makes the results comparable for a given crop even if the true availability is not obtained) had shown, in Mr. Moore's opinion, that quite other conclusions might be drawn. The experiments of Mr. Hartwell, on the other hand, Mr. Moore considered as establishing a definite relation between soil fertility and production, inasmuch as they showed that double the amount of phosphorus was found in the crops fertilized with finely broken bone.

Mr. Davidson called attention to the fact that there was no uniformity in practice as to the size of mesh used in sieving soil samples, although the official method prescribed one-half millimeter. On motion by Mr. Davidson the following resolution was passed:

Resolved, That Committee A on recommendations be requested to consider the question of size of mesh of sieve to be used in preparing samples of soil for analysis.

PLANT GROWTH AS INFLUENCED BY SOIL ACIDITY.

By F. P. Veitch.

Some recent observations and experiments are deemed worthy of record as a contribution to the question of the effect of soil acids on economic crop production.

On a piece of land that to the writer's knowledge has not been cultivated for seventeen years, five plots, each a yard square, were laid out. The native vegetation consisted of bent grass, stunted golden rod, and wild vetch; bent grass predominating. The total apparent acidity by the lime-water method was 800 and by the sodium chlorid method it was 328 parts per million.

The surface 4 inches of each plot was removed, passed through a screen of one-half inch mesh, and with each was incorporated 40 grams of a fertilizer made by mixing 125 grams of dicalcium phosphate, 50 grams of sodium nitrate, and 25 grams of potassium chlorid. Plot No. 1 received no lime; plot No. 2 received 30 grams of lime (CaO), calculated to neutralize the acids as determined by the sodium-chlorid method; plot No. 3 received 60 grams of lime, complete neutralization; plot No. 4, 120 grams, double neutralization; and plot No. 5 received 240 grams of lime, or enough to neutralize four times the natural acidity of the soil. After thoroughly mixing, the soils were returned to their respective plots, and three subplots, each 1 foot by 3 feet, of red clover, alfalfa, and cowpeas, respectively, were planted on each plot. The alfalfa subplots were inoculated with soil from an alfalfa field. The clover and cowpea plots were not inoculated. After planting, the plots had the following reactions:

No. 1, acid, 700 parts per million.
No. 2, acid, 300 parts per million.
No. 3, alkaline.
No. 4, alkaline.
No. 5, alkaline.

At planting plot No. 1 appeared to be the dampest and No. 5 the driest. For three weeks after germination all crops were best in plot No. 1 and became poorer in the order named, plot No. 5 being the most backward. After this time plots 2, 3, and 4 gradually improved, all passing No. 1, with 3 and 4 showing more growth than No. 2. All plants on plot No. 1 were very yellow and did not assume a good color at any time. Alfalfa was an absolute failure on this plot, never getting more than 1½ inches high. Plants on plot No. 2 were also decidedly yellow, while on Nos. 3 and 4 the color was dark green. Alfalfa and clover made no growth on plot No. 5, the large amount of lime in the presence of the large amount of fertilizer used appearing to burn them up. Cowpeas were much injured at first, germinating and growing much more slowly than on other plots; at the end of the season, however, the plot had caught up with the others.

The dry weights of the several crops are given in the following table:

Table I.—*Dry weights of the three crops on five plots.*

Plot No.	Clover.	Cowpeas.	Alfalfa.
	Grams.	*Grams.*	*Grams.*
1	55.0	430.0	00.0
2	120.5	550.0	33.0
3	125.5	870.0	22.0
4	115.5	970.0	33.0
5	00.0	970.0	00.0

The alfalfa on plot No. 3 was badly damaged by moles, and the weight given does not represent the true crop. Judged by appearance, it was fully the equal of plots Nos. 3 and 4.

Nodules on the roots of alfalfa and clover were few—too few to detect any marked difference in the plots. They were plentiful on cowpea roots on all plots, being more numerous and larger on the limed plots. On plots Nos. 1 and 2 the roots of clover died after cutting, while on Nos. 3 and 4 they remained alive and started to grow again.

Cowpeas gave the best results on plots fully neutralized, but the increase from the completely over the partially neutralized plots is but small in the case of red clover. The yield of alfalfa was so small in all cases that it is evident that some unconsidered factor controlled the yield. Failure may have been due to the fact that the soil was neutralized but 4 inches deep or to the large quantity of soluble salts applied. On the whole the writer is convinced that the preparation of the ground, addition of fertilizer and lime, and the planting of the seed all in one day was a mistake. The fertilizers and lime should have been allowed to become more a part of the soil before the seed was planted. The larger yield of cowpeas on plots 4 and 5 may have been due to the more perfect neutralization of the soil of these plots. It is difficult to mix thoroughly 60 grams or even 100 grams of lime with 300 pounds of soil. Cowpeas are extensively grown in the South on acid soils and are generally regarded as quite resistant to soil acids. In this case, in the presence of large quantities of nitrates and a good supply of tubercules, neutralization of the acids has doubled the crop.

In pot experiments with a very acid soil consisting of much organic matter mixed with fine sand transplanted lettuce and tomato died in a few weeks in all the pots except those to which enough lime had been added to completely neutralize the acidity. After the failure of these crops the pots were allowed to rest through the late summer and fall, when it was observed that native marsh grass had grown in them. The crops were harvested and weighed only partly cured.

	Grams.
Pot No. 9, no lime	32
Pot No. 10, limed according to sodium-chlorid method	50
Pot No. 11, limed according to lime-water method	85

It appears that even these native grasses were materially benefited by lime, most by liming to alkalinity.

At the Maryland station there is a piece of land upon which an effort has been made to grow alfalfa for the past three or four years. Before sowing alfalfa the first time the land was limed at the rate of about 30 bushels of stone lime per acre. The alfalfa started, but failed after one or two cuttings. Last fall (1904) the land was again limed at the rate of 30 bushels per acre and sowed to alfalfa, which started well. This spring spots on which there was no alfalfa, but sorrel and weeds, began to appear in the plot. Samples taken from these spots (by permission of the director of the station) gave an acid reaction of 600 parts per million by the lime-water method and of 56 parts by the sodium-chlorid method. Samples taken from where the alfalfa was making a vigorous growth were alkaline. The alfalfa both on the alkaline soil and on the acid soil (where there was any) had nodules on the roots. After being cut twice the alfalfa on the whole plot began to fail, and by fall nearly all of the crop was dead and the plot taken by weeds and crab grass. Samples now taken, both where some alfalfa yet remained and where it had completely died during the summer, showed that the soil was alkaline to a depth of 3 inches and was acid below that depth. It seems possible that acidity of the subsoil has prevented the growth of alfalfa, which is one of the most sensitive plants to acids.

In general these results are in favor of the complete neutralization of acids for the production of maximum yields of the crops grown, but the differences in the plot work were not so large as was expected. On larger plots of this soil red clover has absolutely failed to grow, although fertilized with complete fertilizers carrying nitrates, while timothy has made but little growth. Both did fairly well after lime was applied to the soil, even on unfertilized plots.

Through the courtesy of Doctor Thorne samples were obtained from certain of the rotation plots at Wooster, Ohio. The reaction and acidity of these samples by the lime-water method and by a modification (200 cc N/10 sodium-chlorid solution to 20 grams of soil) of the sodium-chlorid method are given in the following table:

TABLE II.—*Reaction of limed soils by two methods.*

Plot No.	Lime treatment.	Total fertilizer applied in two rotations.	Acidity in parts per million.		Crop yields.	
			Limewater method.	Modified sodium-chlorid method.	Corn (average of 3 years).	Hay (average of 2 years).
					Bushels.	*Pounds.*
2	No CaO	640 pounds acid phosphate	1,000	224	41.48	1,703
2	CaO	do			52.53	3,278
3	No CaO	520 pounds potassium chlorid	1,100	224	28.21	2,087
3	CaO	do	Alkaline.	Alkaline.	41.26	2,830
4	No CaO	No fertilizer	1,100	308	29.05	1,841
4	CaO	do	Alkaline.		40.09	2,823
5	No CaO	960 pounds sodium nitrate	800	168	35.77	2,308
5	CaO	do			45.25	3,173
8	No CaO	640 pounds acid phosphate 520 pounds potassium chlorid	1,100	308	44.18	2,133
8	CaO	do	300	56	56.75	3,816
12	No CaO	640 pounds acid phosphate 520 pounds potassium chlorid 1,440 pounds sodium nitrate	800	280	55.30	3,069
12	CaO	do			63.94	3,974
17	No CaO	960 pounds acid phosphate 520 pounds potassium chlorid 480 pounds sodium nitrate	1,100	280	48.98	2,589
17	CaO	do			63.48	3,738
18	No CaO	32 tons of barnyard manure	1,000	364	54.23	3,035
18	CaO	do			64.19	4,028
19	No CaO	No fertilizer	900	364	30.34	1,585
19	CaO	do	500	56	43.55	2,414
24	No CaO	960 pounds acid phosphate 520 pounds potassium chlorid 360 pounds ammonium sulphate	1,400		48.28	1,704
24	CaO	do	Alkaline.		63.60	3,665
29	No CaO	390 pounds basic slag 520 pounds potassium chlorid 960 pounds sodium nitrate	700	102	52.66	2,963
29	CaO	do			58.36	3,317
	Average of unfertilized unlimed plats				29.78	1,252
	Average of unfertilized lime plats				39.85	2,194

As these plots received different fertilizer treatment there are but few cases where conclusions can be drawn as to the effect of varying degrees of acidity. Further than this, all the crops that have been grown except red clover offer considerable resistance to acidity and will produce good yields on very acid soils. However, the effect of lime on the yield has certainly been marked, and in all cases where the apparent acidity of the unlimed plots has been materially reduced the crop yields have been visibly increased, an increase which, as the evidence indicates, is not due entirely to the direct action of the fertilizer.

The increase of acidity from 1,100 to 1,400 parts per million, due to ammonium sulphate, has had no marked effect on the yield of corn. There is a marked difference, however, from the yield on the completely fertilized plots, the acidity of which is from 700 to 800 parts per million. In no case does the yield of the partially neutralized plots equal that of the completely neutralized plots.

Turning to the hay crop, mixed timothy and red clover, we see that neither acid phosphate nor potassium chlorid, alone or together, has increased the yield, but wherever the acidity has been decreased by nitrate of soda or basic slag the yield has increased, but has not-reached that of the same plots limed. Although plot 17, unlimed, with an acidity of 1,100 parts per million, has produced 2,589 pounds of hay, plot 24, unlimed but receiving receiving its nitrogen as ammonium sulphate, has produced 1,704 pounds of hay, less than the yield of the unfertilized plots.

Barnyard manure, which besides plant food supplies organic matter and bacteria, while increasing the yield greatly on unlimed plots, has not equaled the limed fertilizer plot yield. The increase produced by any combination of fertilizer on unlimed plots has barely exceeded the increase produced by lime alone.

In general it may be said that although fertilizers and manures supplying plant food, lime salts, organic matter, and bacteria produce marked results on all the crops grown—in some cases partly neutralized the natural acidity of the soil—the reaction of the soil was the controlling factor, and the most economic returns were obtained only when the acidity was completely neutralized.

It may be pointed out also that although, through decomposition, the sodium nitrate applied to plots 5, 12, 17, and 29 should have yielded more than enough alkali to render the soils alkaline, as determined by the sodium-chlorid method, the plots still show about half the original acidity, and the yield of clover was not as heavy on these plots as on the limed plots.

Mr. Veitch also submitted by title a paper on The Effect of Fertilizers on the Reaction of Soils, which may be found in Science, for May 4, 1906.

REPORT ON TANNIN.

By H. C. Reed, *Referee.*

Early in the year the referee appointed certain committees, with instructions as to the lines of the work to be pursued. The committees and subjects are listed below:

(1) Evaporation and drying of tannin residues, W. K. Alsop, chairman, H. C. Reed, M. F. Nichols, Chas. Eachus.
(2) Soluble solids filtration, H. T. Wilson, chairman, M. F. Nichols, A. W. Hoppenstedt T. J. Mosser.
(3) Chroming of hide powder, W. K. Alsop, chairman, F. R. Mosbaugh, C. W. Norris, F. H. Small.
(4) Analysis of liquors, F. H. Small, chairman, J. R. Mardick, W. H. Teas, R. P. Cushing.
(5) Acid determination, A. A. Claflin, chairman, F. R. Mosbaugh, C. W. Norris, F. H. Small.
(6) Nitrogen determination, J. H. Yocum, chairman, A. W. Hoppenstedt, J. R. Mardick, A. A. Claflin.
(7) Extraction, W. H. Teas, chairman, Chas. Eachus, Geo. A. Kerr, Harry Gerber.
(8) Parker-Payne method of tannin analysis, W. H. Teas, chairman, W. N. Holmes, H. T. Wilson, Geo. A. Kerr.
(9) Revision of official method of analysis, H. C. Reed, chairman, F. H. Small, W. K. Alsop, W. H. Teas.

Reports have been received from the several committees, with the exception of the committees on acid and nitrogen determinations.

[Note by the Editor.—The detailed reports of the several committees have been printed in full in the "Shoe and Leather Reporter" for November and December, 1905, and January, 1906, and abstracts of the report have appeared in "Hide and Leather" and in "Leather Manufacturer" for November and December, 1905. It is regretted that lack of space prevents the publication of the details of this valuable and exhaustive report in these proceedings, but it is only possible to present the outline of work and the recommendations and proposed official method as offered by the referee for ratification and final adoption in 1906.]

Recommendations.

It is recommended that the following questions be made subjects of collaborative research during the ensuing year:

(1) Soluble solids filtration, with especial reference to the time-contact method, so termed, in conjunction with the temperature problem.

(2) Analysis of liquors and the effect of the acidity of liquors upon the analysis.

(3) Estimation of acid in tan liquors, with a view of improving the present method.

(4) The influence of acidity and alkalinity upon the chroming of hide powder and upon the subsequent analysis. The elimination of the sulphate factor and the merits of a fully or partially chromed prepared hide powder.

(5) Extraction, for the purpose of confirming or rejecting the recommendations of the referee.

(6) The Parker-Payne method of tannin analysis.

(7) Estimation of nitrogen in leather and tan liquors.

It is further recommended that the following methods and processes be adopted provisionally:

(8) The chroming of hide powder by the addition of the entire amount of chrome alum at one time.

(9) Limiting the moisture content of wet chromed hide powder used for analysis between 70 and 75 per cent.

(10) The analysis of liquors as recommended by the referee.

(11) The form of apparatus known as the combined evaporator and drier.

(12) And it is finally recommended that an official method be drawn up from the present method, including the provisional methods recommended in this year's report. Draft of such a method follows:

PROPOSED OFFICIAL METHOD FOR TANNIN ANALYSIS.

I. Crude materials.

(1) *Moisture determination.*—Upon receipt of sample, grind promptly and dry 10 grams in the manner, and for the period specified for evaporation and drying in extract analysis.

(2) *Preparation of sample for extractions.*—Sample must be dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass a sieve of 20 meshes to the inch (linear).

(3) *Amount of sample and proportion of water for extraction.*—For fresh materials the amount of sample and proportion of water for extraction should be such as to give between 0.35 and 0.45 gram tannin per 100 cc of solution. For spent materials this proportion should be approximated as closely as practicable.

(4) *Extraction of sample.*—Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued till a portion tested with gelatin salt solution fails to give a precipitate. At least 400 cc of the first portions of extractive solution should be removed and not subjected to further heating. Thin layer of cotton must be used in order to prevent fine material passing over

(5) *Analysis.*—After extraction and dilution, solutions must be heated to 80° C. and analysis conducted as per official method for extracts. In case of weaker dilutions than the official method specifies the amount of hide powder must be reduced in proportion to the reduction in tannin. Ten grams of the air-dried sample should be dried as in (2), to determine moisture content of the portion extracted, and the analysis calculated and reported upon a "dry" basis.

II. Analysis of extracts.

(6) *Amount and dilution for analysis.*—Fluid extracts must be allowed to come to room temperature, and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from 0.35 to 0.45 gram tannin per 100 cc of solution, dissolved in exactly 900 cc of distilled water at 80° C., and made up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C.

(7) *Total solids.*—Thoroughly mixed solution, pipette 100 cc into tared dish, evaporate and dry as directed under "Evaporation and drying."

(8) *Soluble solids.*—To 2 grams of kaolin (free from soluble salts) add 75 cc of the tannin solution, let stand 15 minutes, decant as much as possible, add 75 cc of solution, stir, and pour immediately on pleated filter paper No. 590 S. and S., 15 cm diameter. Keep filter full, reject first 150 cc of filtrate, evaporate and dry next 100 cc as per "Evaporation and drying." The portion for soluble solids determination must be as clear as practicable, and evaporation during filtration must be guarded against by covering funnel and receiving vessel for filtrate. The temperature of solution during filtration shall be kept between 20° and 25° C.

(9) *Non-tannins.*—A quantity of hide powder, sufficient for the number of analyses to be made, shall be prepared in the following manner: Digest with 25 times its weight of water till thoroughly soaked. Add 3 per cent of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours and let stand overnight. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chlorid. Squeeze the hide, using a press if necessary, so that the wet hide will contain between 70 and 75 per cent of water. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc of the original solution such quantity of the

wet hide as represents from 12 to 13 grams dry hide. Shake for 10 minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grams kaolin to the filtrate, stir and filter through folded filter (No. 1 F Swedish recommended) of size sufficient to hold entire filtrate, returning till clear. Evaporate 100 cc of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder.

The nontannin filtrate must not give a precipitate with a 1 per cent gelatin 10 per cent salt solution.

(10) *Tannin.*—The tannin content is shown by the difference between the soluble solids and the corrected nontannins.

III. Analysis of liquors.

(11) *Dilution.*—Liquors must be diluted for analysis so as to give as nearly as possible 0.7 gram solids per 100 cc of solution.

(12) *Total solids.*—To be determined as in extract analysis.

(13) *Soluble solids.*—To be determined as in extract analysis.

(14) *Nontannins.*—To be determined by shaking 200 cc of solution with an amount of wet chromed hide powder, containing 70 per cent to 75 per cent moisture, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc, in grams.	Dry hide powder per 200 cc, in grams.
0.35–.45	8–10
.25–.35	5– 8
.15–.25	2– 5
.00–.15	0– 2

Solutions to be shaken for nontannins as in extract analysis.

One hundred cc must be evaporated as in extract analysis.

IV. Evaporation and drying.

(15) *Evaporator and temperature.*—The method of drying adopted in 1904 shall be continued in force, but it is recommended that all evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer," at a temperature not less than 98° C, in which case the time for evaporation and drying shall be sixteen hours.

(16) *Dishes.*—The dishes used for evaporation and drying of all residues shall be conducted in flat-bottom glass dishes of not less than 2¾ inches diameter nor greater than 3 inches diameter.

V. Determination of total acidity of liquors.

(17) Place 100 cc of the liquor in a 500 cc flask and make up to the mark with water. To 100 cc of diluted liquor in a flask with tube condenser, add 2 grams of chemically pure animal charcoal Heat to boiling temperature with frequent shaking; cool, filter, and titrate an aliquot portion with decinormal alkali.

Provisional methods.

(A) *Soluble solids.*—Stir up 75 cc of the solution with 1 gram of kaolin, pour upon single-plaited filter paper No. 590 S. and S. 15 cm, filter and return filtrate for one hour, keeping filter full. Have cooled a sufficient portion of the original solution to 20° C. and after removing solution from the filter proceed with filtration of cooled solution discarding at least 10 cc of the filtrate and collecting the first 100 cc thereafter coming clear.

(B) *Analysis of liquors.*—Make up solutions for analysis to contain 0.35–.45 gram, tannin per 100 cc, dilutions being made with water at 80° C. In each case evaporate such an aliquot portion as will give a residue for soluble solids of approximately from 0.7 to 0.8 gram.

Determine soluble solids as in provisional method A.

Determine nontannins as in the official method.

In conclusion the referee desires to express his keen appreciation and sincere thanks to all who have so generously and unselfishly contributed to this report, and especially to the chairmen of the several committees, who have labored so earnestly during the past year for the advancement of our knowledge, and the betterment of the processes under which we are working.

Mr. Veitch. I wish to say that the work in the Bureau of Chemistry with the continuous extractor, reported on last year,[a] has continued to show higher results on tannin than any other extractor we have used. It is interesting to observe that by this long-continued extraction without continued boiling, there has been no evidence of the destruction of the tannin which has been feared in such procedures.

REPORT ON THE SEPARATION OF NITROGENOUS BODIES IN CHEESE.

By R. Harcourt, *Referee.*

The referee decided to test the method elaborated by Van Slyke and Hart for the separation of the nitrogenous bodies in cheese. This method is based on the results of much painstaking work done at the Geneva Experiment Station and was given in Dr. Van Slyke's report as referee on separation of nitrogenous bodies before this association in 1902.[b]

To obtain uniform samples the cheese used was cut into fine particles, thoroughly mixed, and all the sample bottles filled immediately. The following letter of instructions and outline of method to be followed in the analytical work was sent with the samples:

May 5, 1905.

Dear Sir—In accordance with your expressed willingness to cooperate in the work of testing the method of Van Slyke and Hart for the separation of nitrogenous bodies in milk and cheese, I am sending you a prepared sample of cheese for this work. Because of the uncertainity of the action of the various preserving substances upon the different compounds which we wish to separate, no preservative has been put in the cheese. I would, therefore, ask you to keep the sample in cold storage until you are ready to use it, and, if at all possible, to commence the analysis about the 25th of this month. The cheese from which the samples were taken was within a few days of eleven months old, and was of No. 1 quality. * * * The method of sampling, given on the sheets, can not of course be followed in this case. All that need be done is to thoroughly mix the contents of the bottle before weighing from it. In reporting results, will you please mention at what date you made the analysis. I would much prefer that it be made at the time mentioned, but if made later, please report the date on which it was made.

Trusting that you will be able to make a full report, I remain,

Yours, very truly,

R. Harcourt,
Referee on Separation of Nitrogenous Compounds in Milk and Cheese.

It is observed that determination No. 11, of the method, as given in Bulletin No. 73, reads "Determination of nitrogen in the form of unsaturated paracasein lactate," but according to the conclusions given in Bulletin No. 261 of the New York station (Geneva) Van Slyke and Hart now call the compound extracted with a 5 per cent salt solution "free" paracasein, not "unsaturated" paracasein.

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 90, p. 212.

[b] Proceedings of the Nineteenth Annual Convention, U. S. Dept. Agr., Bureau of Chemistry, Bul. 73, p. 87.

Eleven chemists requested samples, eight of whom were able to complete the work and sent in reports. Dr. B. B. Turner analyzed two samples and E. G. de Coriolis, one of my assistants, also analyzed two samples. The eleven reports are embodied in the following table:

Results of cooperative analyses of cheese.

ANALYZED LATTER PART OF MAY.

Analyst.	Total nitrogen.	Water soluble nitrogen.	Salt soluble nitrogen.	Paranuclein.	Coagulated by heat.	Caseoses.	Peptones.	Amido acids.	Ammonia.
E. G. de Coriolis, Guelph,	4.55	1.428	2.391	0.056	....	0.322	0.084	[a] 0.966	
Ontario	4.56	1.428	2.352	.064	....	.333	.065	.966	
F. S. Shiver, Clemson College, S. C	4.87	1.99	1.70	.056	0.014	.366	.094	1.21	0.25
E. B. Holland, Amherst,	4.61	1.62	1.90	.11	....	.45	.05	.92	.09
Mass	....	1.66	2.02	.15	....	.41	.07	.94	.09
C. B. Ellis, Ames, Iowa	4.40	1.68	1.81	.097	....	.022	.01	1.09	.443
J. P. Street, New Bruns-	4.60	1.55	1.35	.14	.02	.15	.01	.97	.26
wick, N. J	4.62	1.56	1.35	.15	.01	.12	....	....	.27
C. W. Jones, Fayetteville, Ark	4.44	3.18	1.05	.18	....	....	....	1.05	.49

ANALYZED LATTER PART OF JULY.

Analyst.	Total nitrogen.	Water soluble nitrogen.	Salt soluble nitrogen.	Paranuclein.	Coagulated by heat.	Caseoses.	Peptones.	Amido acids.	Ammonia.
E. G. de Coriolis, Guelph,	4.59	1.422	1.98	0.031	....	0.395	0.032	[a] 0.984	
Ontario	4.52	1.441	1.99	.031	....	.398	.024	.984	
Dr. B. B. Turner, Storrs, Conn.:									
Sample 1	4.46	1.78	.95	.03	....	.23	.23	1.13	0.16
Sample 2	4.55	1.77	.53	.05	....	....	[b].12	1.215	.155
A. W. Dox, Storrs, Conn	4.52	1.76	.61	.15	....	.23	.07	1.15	.17

ANALYZED LATTER PART OF SEPTEMBER.

Analyst.	Total nitrogen.	Water soluble nitrogen.	Salt soluble nitrogen.	Paranuclein.	Coagulated by heat.	Caseoses.	Peptones.	Amido acids.	Ammonia.
A. H. Knisely, Corvallis, Oreg	4.37	2.03	0.47	0.028	0.006	0.24	0.028	1.481	0.195
	....	1.94	.47	.022	.008	.22	....	....	.209
	....	1.95	....	.020	.006	.23	....	....	.209

ANALYZED LATTER PART OF OCTOBER.

Analyst.	Total nitrogen.	Water soluble nitrogen.	Salt soluble nitrogen.	Paranuclein.	Coagulated by heat.	Caseoses.	Peptones.	Amido acids.	Ammonia.
F. W. Robison, Michigan [c]	4.323	1.998	0.274	Trace.	0.014	0.425	Trace.	1.428	0.126

[a] The ammonia determinations were not satisfactory.
[b] Assuming same amount of caseoses as in sample No. 1 (Turner).
[c] The results were not received until after the report was prepared.

COMMENTS OF ANALYSTS.

C. W. Jones: The sample was kept on ice until May 22, when the analysis was begun. The work was not completed until the 12th of June, and it is possible that there were some bacterial changes as the solutions were kept in a warm room. However, I did not observe any growth of bacteria until after the analysis was completed. In making the water-soluble and the salt-soluble extractions a small amount of white curdy matter collected with the fat and was discarded with it. The cotton filters did not work quickly, taking sometimes over half a day to make filtrations.

In determining the paranuclein the solution was treated according to directions and heated at 50° to 55° C. for four hours and filtered. As the filtrate was not clear it was again heated at the same temperature for four hours and filtered. Even then the filtrate was still somewhat cloudy.

B. B. Turner: I send the results of the analysis of the two samples of cheese sent to Mr. Bosworth and myself. Mr. Bosworth having left this institution, his successor, Mr. A. W. Dox, M. S., analyzed one and I, independently, analyzed both. The difference between the analysis of the two samples may be in part due to the length of time they were in the laboratory. Both were kept in cold storage (about 40° F.) until the work was commenced, July 14. They remained in the hot laboratory several days, with the result that probably the second sample ripened more than the first. I must also point out that

I found the extraction with 500 cc of water, as called for (usually in four portions), was by no means complete. A further extraction with 500 cc of water increased the soluble nitrogen in one case by 0.154 per cent and in another by 0.217 per cent.

F. S. Shiver: The work was done at the time you suggested. Considerable difficulty was experienced in both the aqueous and salt extracts. The determination of paranuclein and caseoses was not very satisfactory.

E. B. Holland: The analysis was begun on May 22. In the estimation of nitrogen in the form of paranuclein a clear supernatant liquid could not be obtained. By keeping the solution at 50° C. for several hours and allowing it to stand over night it filtered clear.

A. L. Knisely: During the summer the cheese was kept in a storeroom, the temperature of which usually ranged from 55° to 65° C. The sample of cheese was opened and the analysis started on September 25. A determination of total nitrogen in the cheese at the top of the bottle gave 4.84 per cent, while that at the bottom gave only 4.21 per cent. I made this determination because I noticed that the fat had partially melted and settled to the bottom of the sample of cheese. The mixed sample gave 4.37 per cent of nitrogen. On filtering the samples through cotton, as suggested, the filtrate was found to be turbid, owing, I presume, to minute particles held in suspension. Upon filtering this through an S. & S. filter No. 588, the filtrate became very clear.

COMMENTS OF REFEREE.

As no means, other than keeping the cheese at a low temperature, was used to check the ripening process, it was felt that the time at which the analyses were made would have considerable influence on the results. To get figures bearing on this point, Mr. E. G. de Coriolis analyzed the cheese at the time specified in the letter and again two months later. Referring to Mr. de Coriolis's results, as given in the previous table, it appears, judging by the amount of water-soluble nitrogen recovered in the two analyses, as though very little advance in the ripening process took place during the two months. About the 1st of October another extraction was made, when it was found that the water-soluble nitrogen had reached 1.840 per cent, the amido acids 1.033 per cent, and the ammonia 0.185 per cent. The cheese had been kept from the time it was bottled until analyzed in cold storage at 40° F.

The reports show that six samples were analyzed during the latter part of May, four in July, and one in September. The latter analysis was made at about the same time as the last extraction by Mr. de Coriolis, just referred to. Mr. Knisely's sample was kept, however, at 15° to 25° higher temperature than the one analyzed at Guelph. The samples analyzed in July were all kept at the same temperature. As was to be expected, the amount of nitrogenous bodies soluble in water increased with the length of time the cheese was kept before the analysis was made, but there is not the close relationship between the different determinations in the various groups that was desired. The length of time the extracts were kept in the laboratory before the analytical work was completed would doubtless increase the quantity of the end products.

Dr. B. B. Turner reports incomplete extraction of the water-soluble nitrogen by the method presented. Work done under my own direction confirms this. A further extraction with 500 cc of water gave the following additional quantities of nitrogen:

	Nitrogen, per cent.
Doctor Turner:	
No. 1 extraction	0.154
No. 2 extraction	.217
Mr. de Coriolis:	
No. 1 extraction	.143
No. 2 extraction	.151

No extractions with additional quantities of the salt solution were made, but uniform results were not secured, and it is quite possible that it was due to incomplete extraction.

Another point tested was the completeness of the separation of the water-soluble extract by the absorbent cotton filter. To check this point a portion of the filtrate obtained in the usual way was filtered through a thick pad of asbestos on a Hirsch filter and nitrogen determined before and after the second filtration. Three extractions were made for the purpose of studying this point, the results of which are as follows:

	Nitrogen per cent.
I. Filtered through cotton alone	1.422 1.441
Filtered through cotton and asbestos	1.410 1.410
II. Filtered through cotton alone	1.480 1.490
Filtered through cotton and asbestos	1.360 1.365
III. Filtered through cotton alone	1.460 1.470
Filtered through cotton and asbestos	1.375 1.365

In the first extraction the absorbent cotton appears to have made a fairly complete separation of the soluble nitrogen; but in the other two cases there is about one-tenth per cent less nitrogen in the portion filtered through the asbestos. Further, filtering through the asbestos pad removes the fat globules and leaves a perfectly clear filtrate, which is much easier carried through the after work.

The cause of the comparatively wide variations in the quantity of the end products was doubtless largely due to the length of time the solutions were kept in the warm laboratory before the analytical work was completed. The influence of this factor on the results was not studied as it was felt that the limited time which could be devoted to the matter would be better employed in studying the question of extraction and filtration.

In conclusion, it may be stated that the separation of organic bodies, such as we have to deal with here, is not a simple matter; it is a separation that requires practice and skill in manipulation. Taking into consideration the difficulties in the way of having the samples in uniform condition when the analyses were made and the nature of the separations the results are encouraging.

RECOMMENDATIONS.

It is recommended—

(1) That this work be continued and that special attention be given to the problem of making a complete extraction of water-soluble nitrogenous bodies and to the complete separation of these in filtering.

(2) That the amount of water used in making the extract be increased from 500 cc to 1,000 cc.

(3) That after the fat and insoluble nitrogenous bodies have been removed by the absorbent cotton, the filtrate be passed through a pad of asbestos.

REPORT ON INORGANIC PLANT CONSTITUENTS.

By R. W. THATCHER, *Referee.*

At the seventeenth annual convention of this association, in 1900, G. S. Fraps presented a paper,[a] in which he called attention to the probable loss of sulphur in the ordinary methods of preparing plant ash for analysis, and stated as the results of his comparative analytical work that "It is plain that the determination of sulphur in an ash prepared in the usual way is far from giving any idea as to the sulphur in the plant." Since that time the attention of the referee on ash each year has been devoted chiefly to the study of methods for determining sulphur in plant tissues. As a result of the investigations in 1901 the nitric-acid method proposed by Fraps was adopted as a provisional method by the association.[b]

In 1902, comparisons of this method with Osborne's method of fusion with sodium hydroxid and sodium peroxid showed that the latter gave considerably higher percentages of sulphur than those obtained by the nitric-acid method.[a] This was confirmed by the cooperative work of 1903,[b] which resulted in the adoption by the association of a recommendation "that the peroxid method of determining sulphur be subjected to further study, with a view of substituting it for the nitric-acid method."

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[a] U. S. Dept. of Agr., Bureau of Chemistry, Bul. No. 62, p. 98.

[b] Ibid., No. 67, p. 151.

Last year's work included an extension of the investigation to vegetable materials containing sulphur in thiocyanate form as well as in albuminoid form, and an attempt to apply the methods to a substance containing a known amount of sulphur in organic combination. Owing to the extreme volatility of the compound selected, artificial oil of mustard, for this latter test, unsatisfactory results were obtained. The work showed conclusively, however, that the nitric-acid method, which still stands as the provisional method of this association, did not yield all the sulphur present in the substances examined.[c] The association therefore adopted recommendations for further study of these methods, and a comparison of these with the so-called "absolute" combustion method proposed by Barlow.[d]

In view of these facts, it seemed very desirable for the referee this year to make an effort to get some conclusive evidence in the matter of sulphur determinations in vegetable materials. Hence urgent requests for cooperation in this work were sent out early in the year. Favorable replies were received from eight laboratories. Samples and the following directions for the work were sent to each of these:

DIRECTIONS FOR WORK ON SULPHUR IN PLANT TISSUE.

The samples for the work this year consist of (1) corn meal, (2) ground oats, (3) cotton seed meal, and (4) white mustard. These samples have been thoroughly mixed and are ready for analysis. Determine moisture in each sample, preferably by drying in hydrogen, and report results. Report results of sulphur determinations in per cent of SO_3 on samples as received and on dry matter. Please report the results of your work as early as possible and make such criticisms of the method as your experience would suggest. Apply Methods I and II to each of the four samples, making at least duplicate determinations in each case. Make determinations also by Methods III and IV, if time and laboratory facilities permit.

Method I.—Place 5 grams of material in a 2½ or 3 inch porcelain evaporating dish, add 20 cc of concentrated nitric acid, and heat cautiously on a water bath until all danger of overflowing has passed. Then evaporate almost to dryness, add 10 cc of a 5 per cent solution of potassium nitrate, evaporate to complete dryness, and ignite gently, allow dish to cool, add a few cc of nitric acid, dry rapidly, and ignite cautiously to white ash. Dissolve this residue in hydrochloric acid and evaporate to dryness and heat for some time in an air bath to render silica insoluble. Take up in water containing a little hydrochloric acid, filter to 150 cc or more, and precipitate the sulphuric acid with a solution containing 1 gram of barium chlorid, and complete the determination in the usual way. Make a blank test with the reagents.

Method II.—Weigh out 15 grams of sodium peroxid (free from sulphates) and introduce about three-fourths of it at once into a nickel crucible; convert into hydroxid by adding a little water and boiling, preferably over an alcohol lamp, until excess of water is completely driven off. Allow the hydroxid to cool until pasty and stir 2 grams of material into it as quickly as possible; heat cautiously until danger of foaming has passed, adding the remainder of the peroxid in small portions from time to time to complete the oxidation. The fused mass, after cooling, is to be dissolved in water, an excess of hydrochloric acid added, evaporated to dryness and heated in an air bath to render silica insoluble. Take up the residue in water containing a little hydrochloric acid, filter and wash to about 400 cc and precipitate the sulphuric acid as before. Make a blank test with the reagents.

Method III.—The Barlow-Tollens "absolute" combustion method (Journal of the American Chemical Society, vol. 26, No. 4, pp. 341–367).

Method IV.—The chromyl-chlorid method proposed by Pozzi-Escot (Experiment Station Record, vol. 16, No. 2, p. 129).

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. No. 73, p. 18.

[b] Ibid., No. 81, p. 229.

[c] Ibid., No. 90, p. 153.

[d] J. Am. Chem. Soc., 1904, *26:* 341.

Results of Cooperative Work.

The laboratory of the Bureau of Standards requested the permission of the referee to apply other methods than those outlined above on the samples sent out, which was most heartily granted. The report of this work, together with that of five other laboratories which submitted results, is included in the tables below.

The results of the determinations of moisture reported by the different analysts are reported in Table I. The results of the determinations of sulphur calculated as SO_3 on the basis of water-free material are reported in Tables II to V.

Table I.—*Moisture in samples.*

Analyst.	Corn meal.	Ground oats.	Cotton-seed meal.	White mustard.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
E. S. Fulton, Amherst, Mass	13.36	9.67	6.61	7.48
H. J. Reese, Bozeman, Mont	13.34	9.31	6.25	6.78
H. C. P. Weber, U. S. Bureau of Standards, Washington, D. C.	13.19	9.84	6.26	6.90
A. T. Charron, Ottawa, Canada	12.90	8.63	5.91	6.57
W. R. Bloor, Pullman, Wash	12.51	10.02	7.40	6.32
R. W. Thatcher, Pullman, Wash	12.00		7.27	6.27
Average	12.88	9.49	6.62	6.72

Table II.—*Determinations of sulphur, sample No. 1, corn meal.*

[Results calculated to water-free basis.]

Analyst.	Method I.	Method II.	Method III.	Parr's calorimeter.	Carius.
	Per cent.	*Per cent.*	*Per cent.*		*Per cent.*
E. S. Fulton, Amherst, Mass	0.242 .238	0.307 .346			
H. J. Reese, Bozeman, Mont	.263 .314				
O. M. Shedd, Lexington, Ky	.187 .124	.323 .307			
H. C. P. Weber, U. S. Bureau of Standards, Washington, D. C		.271 [a] .243	0.264		No ppt. Do. 0.320
A. T. Charron, Ottawa, Canada	.309				
W. R. Bloor, Pullman, Wash	.235 .243	.372 .387			
R. W. Thatcher, Pullman, Wash	.235 .274	.365 .357 [a] .351 [a] .332	.372 .359		
Average	.242	.330			

[a] Made without evaporation for dehydration of silica.

TABLE III.—*Determinations of sulphur, sample No. 2, ground oats.*

[Results calculated to water-free basis.]

Analyst.	Sulphur as SO_3.				
	Method I.	Method II.	Method III.	Parr's calorimeter.	Carius.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
E. S. Fulton, Amherst, Mass	0.343 .327	0.364 .374			
H. J. Reese, Bozeman, Mont	[a].571 .376				
H. C. P. Weber, U. S. Bureau of Standards, Washington, D. C	.345	.344	0.424	0.369	0.294 .276 .309
A. T. Charron, Ottawa, Canada	.321				
R. W. Thatcher, Pullman, Wash	.326 .299	.420 .440	.417		
Average	.332	.381			

[a] Omitted from the average.

TABLE IV.—*Determinations of sulphur, sample No. 3, cotton-seed meal.*

[Results calculated to water-free basis.]

Analyst.	Sulphur as SO_3.				
	Method I.	Method II.	Method III.	Parr's calorimeter.	Carius.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
E. S. Fulton, Amherst, Mass	1.000 .971	1.387 1.454			
H. J. Reese, Bozeman, Mont	1.154 [a].825				
O. M. Shedd, Louisville, Ky	.990 1.045	1.302 1.250			
H. C. P. Weber, U. S. Bureau of Standards, Washington, D. C		1.409 [b]1.418	1.386	1.115	1.220
A. T. Charron, Ottawa, Canada	1.442	1.440			
W. R. Bloor, Pullman, Wash	1.190 1.167	1.390 1.410			
R. W. Thatcher, Pullman, Wash	1.169 1.145	1.480 1.484 [b]1.489 [b]1.453	1.500 1.465		
Average	1.127	1.413			

[a] Omitted from the average.

[b] Made without evaporation for dehydration of silica.

TABLE V.—*Determinations of sulphur, sample No. 4, white mustard.*

[Results calculated to water-free basis.]

Analyst.	Sulphur as SO_3.				
	Method I.	Method II.	Method III.	Parr's calorimeter.	Carius.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
E. S. Fulton, Amherst, Mass	3.852 3.948	4.515 4.451			
H. J. Reese. Bozeman, Mont	2.871 [a] 1.641				
O. M. Shedd, Lexington, Ky	2.879 2.636	4.116 4.000			
H. C. P. Weber, U. S. Bureau of Standards, Washington, D. C		4.457 [b] 4.437	4.489	4.044	3.915 3.665 4.248
A. T. Charron, Ottawa, Canada	4.479	4.125			
W. R. Bloor, Pullman, Wash	4.260	4.390 4.360			
R. W. Thatcher, Pullman, Wash	3.912 4.010	4.664 4.639 4.643 [b] 4.651	4.663 4.620		
Average	3.650	4.397			

[a] Omitted from the average.

[b] Made without evaporation for dehydration of silica.

COMMENTS OF ANALYSTS.

E. S. Fulton: No data is offered on the chromic acid method as nothing satisfactory was obtained.

H. J. Reese: All samples were weighed from weighing bottles. Moisture was determined by weighing in open glasses. In the Fraps process, I would suggest the use of a tall beaker instead of a low casserole when adding the nitric acid, as it boils over even in the cold. My ignitions were performed in a clean muffle out of contact with flames. We did not have any sodium peroxid free enough from sulphates to work with, so did nothing with the method.

O. M. Shedd: My results are on samples as received. It was my intention to determine moisture, but owing to an unexpected absence from the station I did not have the opportunity. (Note by referee.—Mr. Shedd's results, as reported in the tables above, were calculated to the water-free basis, using the average moisture content given in table No. 1.) Method I was modified by using three successive portions of 3 cc each concentrated nitric acid on the ash, igniting strongly for fifteen minutes after each addition of acid. The white residue was dissolved in 5 cc of hydrochloric acid, evaporated to dryness and heated six to eight days in a water bath to render silica insoluble. In ignition gasoline and alcohol were used. Method II was carried out as directed, except that after solution of the fused mass in hydrochloric acid it was evaporated to dryness and heated on a water bath four to five days to render silica insoluble.

F. T. Shutt (*reporting Mr. Charron's results*)*:* The peroxid method does not commend itself to me for the reasons that I gave to the association some years ago. Our experiments this year do not lead me to alter my opinion.

W. A. Noyes (*reporting Mr. Weber's results*)*:* The low results by the Carius method are, I think, due in part to insufficient heating, but they indicate that there is danger of such low results in case of samples containing such small percentages of sulphur. The first two Carius determinations under each substance were made by heating to about 230°–250°. The third in each case was made by heating about 4 hours to 250°, relieving pressure, and then heating above 300° for several hours longer. The results by the explosion method are also low and, I presume, could be improved by a further study of the method. The method has the advantage of being a very quick one. Method II can be very considerably shortened and will still give accurate results, if the evaporation to dryness for the removal of silica is omitted. In the results reported by this method the first determination was made by evaporating to dryness to render silica insoluble as per directions. The second figures were obtained without evaporations. The difference between the two are in opposite directions in various determinations. We consider Method III as the most reliable. Moisture was determined by heating to 95°–98° in hot-water oven to nearly constant weight, this usually taking 5–6 hours' heating.

W. R. Bloor: Method II gives much higher results and is much easier of application than Method I. Moisture determinations were made by drying in hydrogen to constant weight.

REMARKS BY REFEREE.

The results of the cooperative work this year prove conclusively that the nitric acid method does not yield all the sulphur present in plant tissues. Results by this method in the hands of different analysts, and even sometimes of the same analyst, are discordant, probably because of unequal losses of sulphur under varying temperatures of ignition. One of the cooperating chemists this year was able to obtain as much, or a little more, sulphur by this method as by the peroxid method, probably because of greater care in ignitions.

The peroxid method gives higher results. That the results are correct, representing the total sulphur of the substances examined, would appear to be demonstrated by the close agreement of the results by this method with those of the totally different oxygen combustion method (Method III) in the hands of two of the cooperating analysts. Furthermore, recent articles in current chemical literature by Neumann and Meinertz[a], Pennock and Morton[b], Le Clerc and Dubois[c], and Dubois[d] show that the peroxid method is being quite generally accepted as the most accurate and feasible method of those yet proposed. Several modifications in details of operation have recently been suggested, but the general principle of the method seems to be very generally satisfactory. The results from this method on the several samples by the different analysts do not show as close agreement as might be desired, but this is doubtless due to lack of experience with the method on the part of the several chemists and, in some small degree, at least, to differences in factors for calculation to water-free basis due to different methods employed for the moisture determinations.

Method III, combustion in oxygen in a specially arranged combustion tube, as suggested by Barlow, has proved very satisfactory this year to the two chemists who used it upon the association samples. It has the usual disadvantage of combustion-tube methods in amount of time and attention required, but is easily carried out and gives very satisfactory results. It possesses the additional advantage of making it possible to determine the volatile or organic sulphur and the nonvolatile or inorganic sulphur on the same weighed sample and in a single operation.

None of the cooperating chemists were able to obtain any satisfactory results on the association samples by the chromyl-chlorid method this year. It appears probable that this method is not well adapted to miscellaneous agricultural plant tissues.

RECOMMENDATIONS.

It is recommended—

(1) That the provisional nitric-acid method for sulphur in plants be dropped.

(2) That the peroxid method be adopted as a provisional method for sulphur in plants, as follows:

Weigh out 15 grams of sodium peroxid (free from sulphates) and introduce about three-fourths of it at once into a 100 cc nickel crucible; convert into hydroxid by adding a little water and boiling, preferably over an alcohol lamp, until excess of water is completely driven off. Allow the hydroxid to cool until pasty and stir 2 grams of material into it as quickly as possible; heat cautiously until danger of foaming has passed, adding the remainder of the peroxid in small portions from time to time to complete the oxidation. After fusion is complete allow crucible to cool, dissolve contents in water, transfer to a beaker, and add a slight excess of hydrochloric acid. Heat to boiling, filter if not perfectly clear, dilute to about 400 cc, and add 10 cc of a 10 per cent solution of barium chlorid. Let stand overnight, filter, and weigh the barium sulphate in the usual manner. Make a blank test with the reagents.

(3) That the referee for next year be requested to investigate the Barlow-Tollens method as a means of distinguishing between organic sulphur and sulphur of the ash.

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[a] Zts. physikal. Chem., *43:* 37.

[b] J. Amer. Chem. Soc., 1903, *25:* 1265.

[c] Ibid., 1904, *26:* 1108.

[d] Ibid., 1905, *27:* 729.

THIRD DAY.

SATURDAY—MORNING SESSION.

REPORT ON POTASH.

By G. S. Fraps, *Referee.*

This report will relate to the following subjects: The determination of water in kainit, the determination of potash in mixed fertilizers, and the phosphomolybdic method for volumetric potash.

Determination of Water in Kainit.

It has been established by the work of the preceding referee that concordant results can be obtained on potash salts by heating to 130° in an oil oven for ten hours. At 100° much lower results are secured. It has not seemed necessary to repeat this work. The water lost at 100° is what may be termed moisture—that is, it is the variable amount of hygroscopic water held by the salt according to atmospheric and other conditions. The water lost at 130° is hygroscopic moisture plus water of crystallization. It is for this association to decide whether they wish to determine the total water, the hygroscopic water, or both.

The preceding referee on potash made the following recommendation merely in order to place the matter before the association:

> That the directions for the determination of moisture in potash salts, sodium nitrate, and sulphate of ammonia given under the determination of moisture, Bulletin 46, page 11, be made to read as follows:
>
> In potash salts, sodium nitrate, and ammonium sulphate heat 2 grams at 130° in an oil oven for ten hours. The loss in weight is considered as moisture.

The writer is of the opinion that the water expelled at 100° should be termed moisture, and the method used to determine moisture in kainit alone should be applicable to kainit in mixtures with other materials. If total water is desired, a separate method can be used. For these reasons the following recommendations are made:

(1) For moisture in kainit and other fertilizing materials, dry 2 grams material five hours in a boiling-water oven.

(2) For total water in kainit (hygroscopic water and water of crystallization) dry 2 grams material ten hours in an oil oven at 130°.

Potash in Mixed Fertilizers.

It has been known to this association for a long time that our official method does not recover all the potash in mixed fertilizers. The referee in 1903 compared (1) the official method, (2) the official method with 20 cc hydrochloric acid, and (3) the same with the addition of 5 cc of hydrochloric acid and substitution of ammonia by caustic soda. He has the following to say in regard to the addition of acid in the official method:

> The acid modification of the official method tends to give higher percentages of potash, but the results are not always satisfactory. The introduction of such a large amount of ammonium chlorid appears to make the method more difficult of manipulation, and while it is believed that the addition of acid is necessary to liberate all the potash, there are other sources of error which partly compensate for what has been gained in this direction. * * * From later work it appears unnecessary to use so much acid (20 cc), in which case one of

the objections mentioned will be partly eliminated and the results improved. The precipitation with ammonia and ammonium oxalate, however, seems to have the effect of holding back a small percentage of the potash.

The referee did not try the official method with 5 cc of hydrochloric acid. It is quite possible that ammonium hydroxid would give nearly the same results as sodium hydroxid in some cases. Mr. Hartwell, of the Rhode Island station, obtained some results on last year's samples in which ammonium hydroxid gave slightly higher results than sodium hydroxid. The point at issue in the method, however, seems to be not so much the sodium hydroxid as the use of the acid.

The work of the referee on potash in mixed fertilizers has been confined to (1) a comparison of the official and modified methods on mixtures of known composition and (2) the determination of the amount of potash extracted from insoluble potash compounds by the modified method.

COOPERATIVE WORK.

Samples and the following directions were sent to all who expressed a desire to cooperate:

Directions for work on potash.

The samples for the association potash work are numbered and described as follows: No. 1, acid phosphate and potash; No. 2, blood, acid phosphate, and potash; No. 3, cottonseed meal, acid phosphate, and potash.

Mix each sample thoroughly before analysis. Make blank determinations on all reagents. Wash the potassium precipitate out of the crucible with hot water after weighing, dry and reweigh.

Please report results as early as possible, and give the referee the benefit of your suggestions in regard to the work. Any modifications of the methods proposed or used should be described in full. The referee will appreciate a statement of any additional work along these lines.

Determine potash (a) by the official method (p. 21, Bul. 46); (b) by the modified method described below; (c) by the phosphomolybdic method described below.

Modified Method.

Boil 2 grams of the sample 30 minutes with 300 cc of water plus 5 cc of concentrated hydrochloric acid. Add a few drops of phenolphthalein and carefully neutralize with caustic soda, free from potash, avoiding a large excess. (The referee uses a 10 per cent solution.) Precipitate the lime with ammonium oxalate and complete the determination as by the official method. Five cubic centimeters of platinum solution of such strength that 1 cc precipitates 1 per cent of potassium oxid should be sufficient to precipitate all the potash, as it is unnecessary to use sufficient platinum to combine with all the soda.

Phosphomolybdic Acid Method.

Reagents.—Nitric acid wash, 5.5 cc nitric acid (1.40 sp. gr.) in 1,000 cc water. Sodium nitrate wash, 5 grams sodium nitrate per 1,000 cc water. Phosphomolybdic acid solution, 100 grams phosphomolybdic acid (Kahlbaum) in 750 cc water and 250 cc nitric acid (1.40 sp. gr.). Standard solutions, standard caustic potash and nitric acid prepared for the volumetric phosphoric acid. One cubic centimeter of potassium hydroxid is equal to 1.655 mg potassium oxid.

Determination.—Proceed as in the modified official method, using 25 cc of solution, until the ignition to remove ammonium salts. Dissolve the residue from the ignition, transfer to a porcelain dish, add 10 cc phosphomolybdic solution, and evaporate to dryness. Add 25 cc nitric acid wash heated to 50° C, allow the solution to cool, filter through an asbestos filter, and wash with sodium nitrate wash. Transfer to an Erlemmeyer flask, add an excess of standard potassium hydroxid, and heat nearly to boiling. Any precipitate adhering to the dish should be washed out with the standard alkali and washed into the flask. When the precipitate is completely dissolved add a few drops of phenolphthalein, and titrate back with standard nitric acid. (Method of Donk, modified.)

G. S. Fraps, *Referee.*
A. L. Knisely, *Associate.*

Results have been received from 8 analysts, representing 6 laboratories. These results on potash in mixed fertilizers are presented in Table I.

TABLE I.—*Comparison of official and modified methods for the determination of potash in mixed fertilizers.*

Analyst.	Sample No. 1.		Sample No. 2.		Sample No. 3.	
	Official.	Modified.	Official.	Modified.	Official.	Modified.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
A. B. Foster, Maryland station	3.37	3.57	2.93	3.19	3.63	3.62
	3.34	3.62	2.95	3.23	3.69	3.62
H. H. Hurt, Bureau of Chemistry, Washington, D. C.	3.06	3.22	2.99	3.16	3.18	3.63
	3.06	3.20	2.99	3.20	3.37	3.66
C. C. McDonnell, South Carolina station	3.00	3.17	3.05	3.35	3.49	3.66
	3.05	3.24	3.04	3.18	3.47	3.68
F. C. Atkinson, South Carolina station	3.07	....	3.06	....	3.61	....
G. S. Fraps, Texas station	2.96	3.19	3.17	3.29	3.45	3.63
	3.06	3.21	3.14	3.29	3.51	3.77
S. M. Robertson, Virginia-Carolina Chemical Co., Richmond, Va	2.92	3.27	3.04	3.28	3.57	3.76
W. D. Cook, Virginia-Carolina Chemical Co., Richmond, Va	2.94	3.29	3.01	3.26	3.55	3.77
A. L. Knisely, Oregon station	[a]2.44	3.23	3.12	3.42	3.56	3.81
	[a]2.41	3.24	3.13	3.41	3.60	3.80
	[a]2.41	3.25	3.13	....	3.56	....
	[b]2.92	....	[b]3.03	....	[b]3.51	....
	[b]2.85	....	[b]3.02	....	[b]3.54	....
	[b]2.87	....	....	....	....	....
H. D. Haskins, Massachusetts station (Hatch)	[b]2.99	[b]3.46	[b]2.90	[b]3.57	[b]3.38	[b]4.08
Theory	3.34	3.34	3.37	3.37	3.80	3.80
Average of all determinations	3.08	3.28	3.05	3.27	3.52	3.70
Maximum	3.37	3.62	3.17	3.42	3.69	3.81
Minimum	2.92	3.17	2.93	3.16	3.18	3.62
Difference	.49	.45	.24	.26	.51	.19

[a] Omitted from average.

[b] Results received too late to be included in average.

COMMENTS OF ANALYSTS.

F. C. Atkinson: I was unable to obtain concordant results by the modified method, and therefore prefer to withhold the figures. The percentages varied from 0.1 to 0.3 per cent higher than those given by the regular Lindo-Gladding method.

F. P. Veitch: In the modified method I see no necessity for very careful neutralization of the acid with soda, as it is only important not to use a large excess.

C. C. McDonnell: Potassium platinum chlorid precipitate was filtered on a small filter paper, dissolved in hot water, evaporated to dryness, and weighed in a platinum dish.

COMMENTS OF REFEREE.

The modified method gives accurate results, which are nearer the theoretical figures than those given by the official method, as was shown also by the previous referee. The mixtures this year differed from those sent out last year, when tankage was present, while the more soluble organic materials, blood and cotton-seed meal, were used this year. Taking the maximum and minimum of all results, it is seen that the difference is less for the modified than for the official method, that is to say, the determinations come closer together. We must conclude that the modified method gives results more nearly correct than does the official method.

POTASH DISSOLVED FROM SILICATES.

Experiments were made to ascertain how much, if any, potash would be removed from insoluble silicates which might be used as a filler in mixed fertilizers in case the modified method is used.

In regard to the silicates which might be so used, Dr. F. W. Clarke, chemist, U. S. Geological Survey, writes as follows:

The only potassium-bearing silicates which are abundant enough to be considered as "fillers" are orthoclase and muscovite, and I suspect that they are more valuable for other purposes. The Stassfurt potassium salts are, of course, not fillers. All other potassium-bearing minerals are much rarer and can be left out of account in commercial matters.

Dr. H. W. Wiley says:

The following list embraces the most important potash minerals which might be used as such or which occur in other minerals, such as clay, etc., used for fillers in fertilizers: Orthoclase, microcline, leucite, phillipsite, and apophyllite. Of these the last two, being zeolites, will doubtlesss be most attacked by weak acids.

The silicates actually examined were feldspar, leucite, apophyllite, microcline, and muscovite. The analyses were made by the method described in the preceding part of this paper, the precipitate being washed out with hot water and the crucible reweighed after each determination. The results are as follows:

	Per cent.
Feldspar	0.08
Microcline	.08
Leucite	.30
Apophyllite	.27
Muscovite	1.31 1.34
Muscovite (official method)	.91

Only small amounts of potash are dissolved from these minerals by the modified method, except from muscovite, and even in that case only 0.41 per cent more was obtained than by the official method. If 500 pounds of any of these materials were used for a filler in any fertilizer, the maximum increase in the percentage of potash would be 0.08 per cent, having a value of 8 cents a ton at usual prices. Of course, there might be some action of acid phosphate on these silicates, liberating some potash, but this, if it does take place, would affect the results obtained by official method also. The amount of filler that can be used is restricted. Merrill, in "The Non-Metallic Elements" (p. 140), says in regard to mica scraps that "small amounts of inferior qualities are also mixed with fertilizers where it is claimed to be efficacious in retaining moisture." I am inclined to think that the modified method does not open the way for the more extended use of potash-bearing silicates as a filler, as the amount of potash that could be so added is insignificant.

STATE FERTILIZER LAWS.

The laws of many States require potash to be water soluble. California, Delaware, Florida, Illinois, Indiana, Maine, Maryland, Massachusetts, Michigan, Mississippi, Missouri, New Hampshire, New Jersey, New York, Ohio, Pennsylvania, Rhode Island, Texas, Vermont, Virginia, Wisconsin, and West Virginia require either "potash soluble in water" or "potash soluble in distilled water." In Connecticut and Kentucky the statement is in terms approved by the director of the experiment station. Alabama, Georgia, Louisiana, North Carolina, and Tennessee merely call for potash. South Carolina requires soluble potash.

The association must consider whether, under laws requiring potash soluble in water or in distilled water, a method requiring the use of 5 cc hydrochloric acid in 500 cc of water can be used. These laws were undoubtedly framed to exclude the potash of insoluble silicates, and it may be argued that a method which does not include such potash, and which gives credit for the water-soluble potash placed in the fertilizer, can be used. This point is one which the referee would like to have fully discussed before the association, as he is in doubt regarding it.

RECOMMENDATION AS TO THE MODIFIED OFFICIAL METHOD.

The modified method appears to be accurate, and more nearly gives credit for all the potash placed in a mixed fertilizer. It does not appear to open the way to the use of silicates bearing potash. On these grounds the referee is willing to indorse the following recommendation of the previous referee, which has gone over to this year under the rules:

That the modified method be adopted as the official method.

On the other hand, the laws of twenty-seven States require the potash to be soluble in distilled water, or water, which was obviously intended to exclude insoluble potash silicates, and may, in the opinion of this association, render inadvisable the adoption of a method requiring the use of a small quantity of hydrochloric acid. Being doubtful in regard to this point, your referee hesitates to give the above recommendation his unqualified indorsement, and hopes that this point will be discussed fully.

THE PHOSPHOMOLYBDATE METHOD FOR POTASH.

This method, as devised by M. G. Donk, is described by him in the proceedings of this association for 1904,[a] to which reference can be made for details. The following details of manipulations were sent to the referee by Mr. Donk:

> Quantitative tests as to the solubility of potassium phosphomolybdate were made only in nitric acid. Qualitative tests were made on sodium phosphate, sodium molybdate, molybdic acid, phosphomolybdic acid, sodium chlorid, calcium nitrate, hydrochloric, sulphuric, citric, acetic and oxalic acids, ethyl and amyl alcohol, solution of ethylic alcohol, amyl alcohol, glycerin, and some others. The organic fluids, though appearing to exert but slight solvent effect on the yellow precipitate, seemed to convert it into the celloidal form, thus rendering it difficult to wash.
>
> The titrations were made hot, an excess of alkali being added to the precipitate in a casserol, warmed, and run back with nitric acid.
>
> The acid and salt solutions exert a solvent effect upon the yellow precipitate increasing with their concentration. The acid and wash solution was made as weak as it was possible to be, and at the same time counteract the hydrolytic tendency of water.

The preliminary work consisted in the determination of the solubility of potassium phosphomolybdate in water and in nitric acid, and in some work regarding the factor to be used.

SOLUBILITY OF THE PRECIPITATE.

The potassium phosphomolybdate was prepared with an excess of potassium chlorid, worked thoroughly with 1 per cent sodium nitrate, dried, and brought in contact with the liquid. After a definite time, 100 cc was drawn off and titrated with the caustic potash used for phosphoric-acid work, when water or sodium nitrate was used, or evaporated to dryness, dried, dissolved and titrated if nitric acid was used. The results are as follows:

TABLE II.—*Solubility of potassium phosphomolybdate in sodium nitrate.*

Sodium nitrate per liter.	Remarks.	Caustic potash consumed per 100 cc.	
		24 hours.	72 hours.
Grams.		*Grams.*	*Grams.*
100	Clear	1.25	3.65
50		.75	2.4
20		.55	2.65
10		.30	1.8
5		.27	.95
0	Turbid	.15	.30
0		.12	....

[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. No. 90, p. 219.

Table III.—*Solubility of potassium phosphomolybdate in nitric acid.*

Nitric acid per liter.	Remarks.	Caustic potash consumed per 100 cc.		
		24 hours.	48 hours.	48 hours (heated to 50° C. and cooled)
Grams.		*Grams.*	*Grams.*	*Grams.*
0	Turbid	0.12	0.17	1.25
5	Clear	.40	1.05	1.40
10	Clear	.94	1.36	1.80
20	Clear	1.04	1.57	1.72

The precipitate is less soluble in water than in any of the solutions in spite of the fact that the latter were clear and the water was turbid. The amount of potassium phosphomolybdate dissolved increases with the time of contact and the strength of the solution. The former action is especially marked if potassium phosphomolybdate is allowed to remain in contact with sodium-nitrate solution for some days, as the solution becomes markedly yellow from the dissolved salt. For this reason the treatment of the wash solution with potassium phosphomolybdate as recommended by Donk was discontinued. It is quite possible that water would give results equally as good or better than the solution of sodium nitrate called for in the directions sent out, but on account of the turbidity of the filtrate, which would be expected, water was not used.

The precipitate is appreciably soluble in water or nitric acid when heated to 50°, and it would be desirable to omit this procedure if possible, but it is believed to be necessary to cause the excess of phosphomolybdic acid and other substances present to go into solution, and by using a small amount of the nitric acid the solvent action on the precipitate is reduced very much.

FACTOR TO BE USED.

In the method sent out, solutions used in volumetric phosphoric acid were required, for the simple reason that they are already present in many laboratories, and new solutions would not be necessary. If desired, solutions of different strength can be used.

To determine the factor, the formula of Gibbs for ammonium phosphomolybdate ($48MoO_3.2P_2O_5.5(NH_4)_2O.H_2O.16Aq$) was used and a similar composition assumed for the potassium salt. The ratio $2P_2O_5$: $5K_2O$ is 1: 1.655, so that, in using the solutions for volumetric phosphoric acid, we multiply phosphoric acid by 1.655 to convert to potash. As pointed out by Mr. McDonnell, this factor is too high. The amount of standard solution required for a known amount of potash using 0.1 gram of potassium chlorid was also determined. As an average of four determinations, the factor 1.646 was obtained. The presence of a small amount of carbonates in the solution is believed to have interfered somewhat with the accuracy of this work.

COOPERATIVE WORK.

A description of the method sent out for trial has already been given. The results reported by the different analysts are presented in Table IV.

TABLE IV.—*Comparison of gravimetric and volumetric methods.*

Analyst.	Sample No. 1.		Sample No. 2.		Sample No. 3.	
	Grav.	Vol.	Grav.	Vol.	Grav.	Vol.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
A. B. Foster, Maryland station	3.57 3.62	3.63 3.53	3.19 3.23	3.20 3.20	3.62 3.62	3.82 3.93
H. H. Hurt, Bureau of Chemistry, Washington, D. C	3.22 3.20	3.00 3.20	3.16 3.20	3.28 3.23	3.63 3.66	3.40 3.50
C. C. McDonnell, South Carolina station	3.17 3.24	3.38 3.41	3.35 3.18	3.38 3.21	3.66 3.68	3.61 3.67 3.71 3.74
F. C. Atkinson,[a] South Carolina station	....	2.99	....	3.01	....	3.59
G. S. Fraps, Texas station	3.19 3.21	3.46 3.11	3.29 3.29	3.52 3.36	3.63 3.71	3.75 [b] 4.08
A. G. Knisely, Oregon station	3.23 3.24 3.25	3.26 3.23 3.25	3.42 3.41	3.54 3.57 3.38	3.81 3.80	3.73 3.63 3.59
H. D. Haskins, Massachusetts station (Hatch) [c]	3.46	3.88	3.57	4.34	4.08	3.71
Average of all determinations	3.28	3.31	3.27	3.32	3.70	3.67
Maximum	3.62	3.63	3.42	3.57	3.81	3.93
Minimum	3.19	2.99	3.16	3.01	3.62	3.40
Difference	.43	.64	.26	.56	.19	.53

[a] Prepared his own phosphomolybdic acid.
[b] Excluded from totals.
[c] Results received too late to be included in totals.

Comments of analysts.

F. C. Atkinson: I do not consider the volumetric method as reliable as the gravimetric method, although fairly concordant figures were obtained. The method is perhaps a little shorter than the gravimetric method, but in my opinion the amount of time saved is insufficient to justify its use in preference to the platinum chlorid method.

A. B. Foster: The results given by the phosphotungstic acid method were not very different from those obtained by the platinum chlorid, but the new method is much slower, and I could see no advantage in using it. In the volumetric method it was found better to use a paper filter and titrate in the porcelain dish in which the residue was evaporated to dryness.

F. P. Veitch: Both Mr. Hurt and myself were favorably impressed with the volumetric method. I do not believe, however, that nitric acid or potassium hydroxid of the strength required or the use of an Erlenmeyer flask for titrating adds to the accuracy of the method.

C. C. McDonnell: The potassium phosphomolybdate precipitate was collected on a small filter and washed with sodium nitrate wash. Filter and precipitate were then transferred to an Erlenmeyer flask, a little water added, and the flask shaken until paper thoroughly broken up.

I have calculated the results using the factor 1.655 as directed, and also by the factor 1.625. [Remark by referee.—In the latter case results are 0.06 per cent lower.] As stated in my letter of June 26, it appears that the theoretical factor is 1.625—that is, assuming the formula of the potassium phosphomolybdate formed to correspond with the formula given by Gibbs for ammonium phosphomolybdate as you have done.

However, it seems that 1 cc of the potassium hydroxid prepared as in the volumetric method for phosphoric acid is not equal to 1 mg P_2O_5 in a precipitate of the above composition. As stated by Pemberton, the formula of the ammonium phosphomolybdate on which this solution is based is $(NH_4)_6(PO_4)_2(MoO_3)_{24}$, which requires 46 molecules of potassium hydroxid to neutralize, using phenolphthalein as an indicator. In ammonium phosphomolybdate of the formula as given by Gibbs, therefore 94 molecules of potassium hydroxid would be required to neutralize. This would give as the equivalent of P_2O_5 in 1 cc of the potassium hydroxid solution, 0.979 mg.

Hence on the potash salt the ratio would be $2P_2O_5 : 5K_2O :: 0.979 : 1.625$.

A. L. Knisely: The volumetric method seems to me to be very promising.

Comments of referee.

The results by the volumetric method, while not so uniform as those given by the gravimetric method, show that it deserves further study. The referee believes that it is particularly promising for soil potash. In the official method, which is long and tedious, there is room for loss of potash by occlusion. If the soil solution can be evaporated directly with the phosphomolybdate reagent, and the resulting precipitate washed and titrated with accurate results, a much quicker method than the present tedious and somewhat unsatisfactory one will be secured. The point of Mr. McDonnell is well taken, and 1.625 is the theoretical factor.

RECOMMENDATIONS.

The referee recommends that the study of the volumetric method be continued, with particular attention to its use in soil analysis.

Mr. Robison, the referee on nitrogen, reported through the secretary of the association that although he had done some individual work on the nitrogen methods according to the recommendations made, no cooperation had been secured and no report on the subject compiled.

Mr. Fuller. I wish to make the following recommendation in regard to the determination of nitrogen:

That in the official Gunning method for the determination of nitrogen the addition of one-half to three-quarters of a gram of copper sulphate, after digesting with sulphuric acid and potassium sulphate for one-half hour, be studied by the referee.

The recommendation was referred to Committee A.

Mr. E. W. Magruder, referee on phosphoric acid, stated that he had no report to present, but suggested that work should be done on the two following points: (1) Determination of the neutrality of the citrate solution, and (2) the determination of iron and aluminum in phosphoric acid, looking to the adoption of an official method for these determinations.

Mr. Gladding. As a commercial chemist I have had special difficulty during the past year in regard to the determination of organic potash in fertilizers. For example, I examine a cargo of beet-sugar residue which has been bought on the basis of the percentage of total potash as determined by the foreign chemists. This being in the form of organic potash, I make the determination according to the official method of this association—i. e., by adding sulphuric acid, igniting, and dissolving the residue in hydrochloric acid. The result is approximately that obtained by the foreign chemist, and all goes well until the importer's chemist reports 1 per cent less potash than I found. Then I must explain that organic potash is available potash, and that the determination of water-soluble potash in the mixed fertilizer will not give as high a result, and the importer is unable to understand why the potash which was considered available before it was mixed with tankage or acid phosphate has become nonavailable. I would therefore beg that some recommendation be made to so modify the potash method as to give credit for the organic potash in mixed fertilizers by incineration at low heat and subsequent solution in acid. In some of the slags the difference between the water-soluble and what is called the available potash is one-fifth of the whole amount, and marked differences are found in garbage tankage and many other materials. It seems to me, therefore, that in the interest of a square deal the methods should be so amended as to give credit for the organic potash in mixed fertilizers as available.

Mr. McDonnell. The question occurs, Is all the potash obtained after incineration and acid solution as available and valuable as the potash salts? This point should be considered before making any change in the methods for obtaining total potash.

Doctor Frear. It must be remembered that some of us as official chemists are required by the State laws to report water-soluble potash, and it is necessary for such chemists to have an official method which may be followed to the letter.

Mr. Davidson. Though we can not say that we shall adopt an official method for determining this organic potash, the association might put itself on record as willing to guarantee that potash in cotton-seed meal, tobacco stems, etc., will be considered as available potash. We might report total and water-soluble potash and leave it to the different States to act upon the matter. I suggest that the matter be taken up by the committee on recommendations.

Mr. Winton. We know that there are potash salts soluble in water that are available, and also that there are other forms not soluble in water but soluble in acid that are at least of inferior availability. Organic potash is unquestionably of value, but if we so modify our method for mixed fertilizers, introducing incineration and dissolving in acid as to give credit for the organic potash, this method will also give credit for other forms soluble in acid which are not available. Until we find some method that will exclude these unavailable forms it seems to me that the small amounts of organic potash must be disregarded in mixed fertilizers.

Mr. Carpenter. We find that we lose 10 per cent of the total potash where only water-soluble potash is determined in mixed fertilizers, which amounts to a large sum of money when a million tons of fertilizer is put out, and I should be glad to see the association take action on the matter as soon as possible.

Mr. Gladding. There seems to be a difference of opinion as to the value of this organic potash, but I think the association committed itself on this point when the method of incineration was adopted for the determination of total potash in cotton-seed meal, etc. It has been said that this method would calculate as available the potash in the form of silicate, etc., but I understand from the referee's report that the silicate of potash was but little affected by the acid treatment. In regard to the State laws, it seems to me that the association should take the position that is scientific and correct in such a way as not to conflict with the State laws but ultimately to bring them also to that position.

Mr. McDonnell. I do not think that we have committed ourselves on the subject of the value of this organic potash. Because we have a method for its determination, it does not follow that it is of equal value in all of the by-products in which it occurs. We certainly are not ready to maintain that total potash in garbage tankage is equivalent in value to water-soluble potash.

Mr. Davidson. It does not seem to me that our method prohibits the use of sulphuric acid and incineration for the determination of total potash in mixed fertilizers. Would not the term "organic compounds" include such mixtures?

Doctor Frear. In interpreting this point it must be remembered that the methods are a series of prescriptions, not prohibitions. I doubt the safety of interpreting them from the opposite point of view.. While I am not contending that there is not much to be said in favor of providing for the potash found in organic combination, I would hesitate, as a chemist responsible for fertilizer-control work, to take any action at this time, though I would be glad to have the matter taken up for careful consideration.

The following resolution offered by Mr. Gladding was referred to Committee A:

> That a method of incineration at low temperature and subsequent solution in dilute acid [for the determination of organic potash in mixed fertilizers] be examined and reported on at the next annual meeting.

Mr. Allen. In North Carolina we always incinerate mixed goods containing cotton-seed meal, etc. It seems to me that if the methods provide for incinerating organic compounds existing alone, and do not prohibit it when they are mixed with other materials, that they should be incinerated.

Mr. Winton. I wish to emphasize the fact that it is generally admitted that the acid-soluble potash is not as valuable as the water-soluble, although it is not worthless. I think we should also bear in mind that it is not only a question of giving credit for organic potash but of giving credit for acid-soluble potash in inorganic materials. Large classes of materials, and those most commonly used in fertilizers, are properly valued by the determination of water-soluble potash and phosphoric acid.

NOTES ON THE USE OF ACETIC AND OXALIC ACID FOR EXTRACTING THE CHARRED MATERIAL IN PREPARING ASH.

By B. L. Hartwell and J. W. Kellogg.

When material is incinerated with a view to retaining in the ash all of the potassium and sodium it is usually advisable to extract the substance obtained by charring at a low heat, with some solvent which shall remove the soluble ash constituents before the charred material is subjected to the higher heat necessary for complete incineration. The method of the Association of Official Agricultural Chemists suggests water or acetic acid for this purpose, depending upon circumstances.

In the analysis of the ash of mixed grasses, principally timothy and redtop, it was found that about 20 per cent, after dehydrating the silica, consisted of material insoluble in hydrochloric acid. Very little "sand" could have been present, for the samples were cut from a compact turf, and the only source of dirt was such dust as may have adhered to the growing plants. Practically no effervescence occurred upon adding hydrochloric acid to this ash, there being sufficient acid radicals other than carbon dioxid to combine with the bases.

It had been our general custom in the preparation of plant ash to char the substance at a low temperature and to extract the charred material thoroughly with hot water, in order to remove alkalies and to aid in the incineration. A single test with the hay showed that 8 per cent of the total amount of potassium and sodium was left unextracted by the hot water, even though the charred material was digested with the same for some time. It seemed, therefore, that it might be desirable in some cases to use an acid in the extraction to guard against the possibility of any volatilization of the alkalies during the final ignition, and dilute acetic acid was given a trial in comparison with the water. It was noticed invariably that the portion of the ash from the charred, extracted material was the browner where the acetic acid was used, indicating that the proportion of iron was greater, due probably to the more thorough extraction of the calcium by the acetic acid, and also that it dissolved with greater difficulty in hydrochloric acid. In a few instances the ash from the extract and that from the charred, extracted material were kept separate, and the total silica determined in each case. The amount of silica was noticeably greater in the extract secured by water than when acetic acid was used.

Chicory tops, carefully brushed to remove all soil which had spattered upon them during heavy showers, yielded an ash which generally contained, after dehydrating the silica, about 6 per cent of material insoluble in hydrochloric acid. In the case of this material there was considerable carbon dioxid in the ash; but it will be noticed that the proportion of insoluble matter is much less than in the ash from hay, in spite of the fact that there was greater liability of contamination by soil in the case of the chicory tops, which were from a hoed crop. In making a comparison of water and of acetic acid for extracting the charred material of the chicory tops, a liberal quantity of the latter, after charring, was mixed and divided into two equal portions, one of which was thoroughly extracted with dilute acetic acid and the other with water. The comparison was, therefore, more exact than in the case of the hay, where the extraction was from two separately charred portions, which may have varied slightly as regards the extent of charring. Eighty-four per cent of the crude ash was obtained from the acetic acid extract, whereas only 50 per cent was in the aqueous extract. Twenty-two per cent of the total silica was found in the acetic acid extract and 3 per cent in the aqueous extract. In this instance a larger proportion of the silica was extracted by the acid than by the water, while with the hay the reverse seemed to be true, owing, perhaps, to the precipitation of some of the soluble silica of the highly siliceous hay and to its retention with the charred material. The ash from the charred chicory tops, exclusive of that from the extract, was browner and dissolved with greater difficulty when acetic acid was used as the extracting solution than when water was employed, as was also true in the case of the hay. It seems likely that the more complete removal of the lime by the acetic acid is a detriment to the final incineration of the charred material from certain plant substances, resulting, as was noticed, in an ash which is more difficult to dissolve in hydrochloric acid.

The total amount of crude ash was invariably greater when acetic acid rather than water was used. This was due in part, at least, to carbon from the incomplete ignition of the acetates in the extracted material, for upon the evaporation of the extract, after combining it with the ash from the charred material, and after subsequent ignition, a more or less blackened mass was obtained which could not be burned to a light-colored ash without increasing the temperature to a degree which might result in volatilization of alkalies.

It seemed as though the objections to the use of acetic acid could be overcome by substituting oxalic acid. The latter, of course, would leave the calcium with the charred material, and, owing to the larger proportion of oxygen to carbon in this acid than in acetic acid, no carbonaceous residue would be left upon ignition. Therefore, a comparison was made between dilute oxalic acid and water for extracting the charred material from hay of similar character to that mentioned previously. Equal portions of the charred material were extracted by the two solutions and the silica in the crude ash from the extract and also from the charred material itself determined separately. From four different samples of hay, 90, 95, 87, and 89 per cent of the total silica were found in the charred mass which had been extracted with oxalic acid, while that left from the extraction of like material with water usually constituted less than 70 per cent of the total silica.

It was thought that the difference in the relative amounts of the various ash ingredients in the charred substance, depending upon whether water or acid had been used in the extraction, might have an influence upon the amount of impurity which is almost invariably contained in the total silica. The insoluble matter in the ash of the charred substance from hay, referred to in the preceding paragraph, was treated, therefore, with hydrofluoric acid to volatilize the silica, and the residue soluble in hydrochloric acid was determined. The grams of residue per 30 grams of four different samples of hay are given below.

TABLE I.—*Comparison of residues per 30 grams of hay obtained by extraction with water and with oxalic acid.*

Extraction.	Sample I.	Sample II.	Sample III.	Sample IV.
	Grams.	*Grams.*	*Grams.*	*Grams.*
"Char" extracted with water	0.0342	0.0203	0.0159	0.0170
"Char" extracted with oxalic acid	.0166	.0150	.0105	.0168

REDUCED TO PERCENTAGES OF INSOLUBLE MATTER FROM WHICH RESIDUES WERE OBTAINED.

	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
"Char" extracted with water	13.3	12.0	9.7	10.0
"Char" extracted with oxalic acid	6.3	6.8	4.6	7.5

These results indicate that the insoluble matter in the ash from hay will contain less nonsiliceous material if oxalic acid instead of water is used for extracting the charred substance. The insoluble matter in the ash from carrots and radishes, however, which was about one-fourth as much as from the hay, yielded no greater residue from treatment with hydrofluoric acid when water was used to extract the charred material than when oxalic acid was used.

When the samples to be analyzed are free from adhering soil it is advisable to treat the insoluble matter of the ash with hydrofluoric acid in order to volatilize the silica which is then represented by the difference in weight, caused by the action of the hydrofluoric acid. The residue may then be dissolved in hydrochloric acid and combined with the main portion of the solution before diluting to a definite volume. This residue is frequently of considerable magnitude, depending upon the nature of the material and the method of ignition, and often causes unsatisfactory parallels and considerable error when included in the total silica, as well as a minus error in the determinations of the nonsiliceous ingredients. If any considerable amount of soil is present with the sample it would be unwise, of course, to use hydrofluoric acid, as suggested above, for the reason that the ingredients of the soil would then be included with the ash constituents and lead to plus errors.

Unless the preliminary ignition has been quite thorough before the charred material is extracted to remove the alkalies previous to complete incineration, the aqueous extract will often be dark colored from organic matter. This is not apt to be the case, however, when oxalic acid is used for extraction.

A complication will arise in the use of oxalic acid in connection with the determination of calcium oxid, unless the oxalates are completely decomposed, for the reason that calcium oxalate will be precipitated with the iron phosphate. Some uncertainty may be felt as to whether the heat required to decompose all of the oxalates, which may be present with a large amount of ash, could lead to any volatilization of alkalies. It seems improbable, considering the combinations in which the alkalies occur at this stage, that they would be volatilized, but the only data which we have bearing upon this point is a comparison of results obtained by using water for extracting the charred material from one portion of a sample, and oxalic acid for extracting the charred material from another portion of the same sample. A single determination only was made in each case and the results are given below.

Table II.—*Comparison of extractions of charred material by water and by oxalic acid.*

[Expressed in grams per 1.25 grams of air-dry material.]

Description of sample.	Potassium and sodium chlorids.		Potassium chlorplatinate.	
	Water.	Oxalic acid.	Water.	Oxalic acid.
Carrot roots:	*Gram.*	*Gram.*	*Gram.*	*Gram.*
Sample 1	0.0937	0.0929	0.0809	0.0803
Sample 2	.1170	.1201	.0718	.0724
Sample 3	.0821	.0819	.0876	.0864
Sample 4	.0744	.0723	.0938	.0925
Carrot tops:				
Sample 1	.1214	.1192	.0597	.0576
Sample 2	.0746	.0748	.0904	.0904
Radish roots:				
Sample 1	.1935	.1918	.3696	.3680
Sample 2	.1696	.1673	.3294	.3246

The above differences are considered within the limit of analytical error for routine work carried on in the manner described, and do not indicate any differences due to the method of extraction. It should be said in this connection that the residues from treating the insoluble matter of the ash with hydrofluoric acid were dissolved in hydrochloric acid and included with the other acid-soluble ingredients of the ash, so that any possible differences which might have occurred from that source would not appear in the above figures.

The amount of crude ash was generally the greater when oxalic acid was used. As would be expected, there were no evidences of carbon left from the decomposition of the oxalates, and it seems probable that the amount of ash was greater because it was more thoroughly carbonated. With hay, where the evolution of carbon dioxid upon the addition of hydrochloric is small, the greater effervescence from the ash prepared with the extraction by oxalic acid could be readily noticed.

In reply to the request for remarks on nitrogen determination Mr. Hartwell stated that he found the modified Gunning method inadequate, if followed strictly as prescribed, all the nitrogen not being obtained in the presence of a large amount of nitrates, and suggested that this point receive the attention of the referee on nitrogen.

Mr. Frear. I have received a number of requests from importers who desire to introduce basic slag in this country that the association take action as to the methods of analysis to be applied to this material. If large quantities of this fertilizer are to be offered in this country I think we shall be confronted by a serious problem in estimating it in mixed fertilizers; in considering the substance alone we have the European practice to guide us; a very different problem is presented by American trade conditions. I offer the resolution that the referee on phosphoric acid take up for report at the next meeting of the association, methods applicable under American conditions to the official examination of basic slag phosphates.

Mr. Leavens. The question of the treatment of acid soils is becoming more and more important throughout the country, not only in northern sections, but also in the Middle States and the South. This has drawn special attention to the value of basic slags for such lands. Its use has been urged by various experiment station directors and chemists, including those of the States of Massachusetts, Rhode Island, Indiana, and California. There seems to be, however, no understanding as to a suitable method for the determination of available phosphoric acid in this material, which I can assure you is to be imported into this country during the coming season.

I have a letter from the California station stating that the association has been urged to adopt some fair method of valuation for this material, a great deal of basic slag being used in that State. It is stated further that the official ammonium citrate method is not used. The use of a 100-mesh sieve for the determination of available phosphoric acid shows that the fine material runs about 80 per cent, a fair gauge of its availability—that is, they recognize that the present methods are not satisfactory.

From both the standpoint of the buyer and the seller, in justice to this valuable material and to progressive agriculture, some definite action should be taken in this matter which has hung fire for several years, the proceedings only showing that the ammonium chlorid citric acid method apparently comes the closest to giving correct results. I do not wish to urge the adoption of this or any other method, but only that some action should be taken.

Although all substances used only as manures are duty free, basic slag, doubtless by an error, labors under the handicap of an import duty of $1 per ton. In view of this fact it is most important that we be able to guarantee a certain per cent of available phosphoric acid in order that the slag may not be doubly handicapped.

I am not here to oppose the phosphate interests of the country—the house with which I am connected manufactures acid phosphate—I simply wish to urge the adoption of a fair method for the determination of available phosphoric acid in this material which is destined to be of great value to the agricultural interests of this country.

Mr. Hartwell. A distinction should be drawn between the value of this material to acid soils because of its alkalinity and its value as containing available phosphoric acid. I made up an artificial mixed fertilizer containing basic slag and found that by the official method only about 51 per cent of the total phosphoric acid was available. I will not undertake to say whether this is all that should be considered as available or not, but we must remember that the accompanying salts have an effect on the solubility, and for the present, until we know more of the value of phosphorus in such mixed materials, we will be doing no injustice by submitting them to the regular method.

The resolution offered by Mr. Frear was passed.

MODIFICATION OF THE METHOD OF DETERMINATION OF PHOSPHORIC ACID.

By A. B. Foster.

Place 2 grams of the sample in an Erlenmeyer flask of 175 to 250 cc capacity, add 10 cc of hot water, allow to stand for half an hour or longer, and add 90 cc of neutral ammonium citrate (sp. gr. 1.1), heated to a temperature of 85°. Then place the flasks in a water bath having a temperature of 65° and hold at that temperature as nearly as possible for half an hour; filter, wash with hot water, saving the filtrate and wash water, cool, shake, and add 10 cc of strong hydrochloric acid; make up to any convenient volume.

Place an aliquot part of this solution in a 150–250 cc beaker and make alkaline with ammonia; if necessary a strong solution of ammonium citrate or citric acid is added to make the solution clear.

Then add magnesium mixture in the usual way and allow the solution to stand four hours, filter, and complete according to the regular procedure. If it is desired to determine insoluble phosphoric acid the residue from the digestion and filtration may be used in the customary way.

My experiment consisted in determinations on 8 samples:

1. Acid phosphate.
2. Acid phosphate.
3. Acid phosphate and potassium sulphate.
4. Acid phosphate and potassium chlorid.
5. Acid phosphate and organic nitrogen.
6. Acid phosphate and nitrate nitrogen.
7. Acid phosphate, organic nitrogen, and potash salts.
8. Acid phosphate, organic and nitrate nitrogen, and potash salts.

Phosphoric acid determinations.

Number of sample.	Total.	Insoluble.	Available by difference.	Available by modified method.	Difference.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent*	*Per cent.*
1	15.52	.96	14.56	14.78	+0.22
	15.59	1.05	14.54	14.70	
2	15.93	1.28	14.65	14.94	+ .27
	15.79	1.18	14.61	14.86	
3	11.40	1.02	10.38	10.47	+ .12
	11.28	.96	10.32	10.39	
4	14.11	1.63	12.48	12.35	− .08
	14.00	1.56	12.44	12.41	
5	11.06	2.22	8.84	8.86	− .06
	11.20	2.23	8.97	8.81	
6	8.34	1.43	6.99	7.01	+ .03
	8.48	1.42	7.06	7.11	
7	8.13	2.07	6.06	6.18	+ .13
	8.27	2.12	6.15	6.30	
8	9.52	1.13	8.39	8.46	+ .11
	9.64	1.26	8.38	8.53	

REPORT ON THE SEPARATION OF VEGETABLE PROTEIDS.

By Joseph S. Chamberlain, *Associate Referee.*

Owing to routine work the associate referee was not able to conduct the cooperative work on the separation of the proteids of barley and malt which had been planned, and only recently has he been able to study these methods in connection with the investigations on barley and malt that are being carried on in the Bureau of Chemistry. The only recommendation that can be made, therefore, is that the following method by Horace T. Brown [a] be used for the estimation in barley and malt of the total amount of nitrogenous substances soluble in water.

THE ESTIMATION IN BARLEY AND MALT OF THE TOTAL AMOUNT OF NITROGENOUS SUBSTANCES SOLUBLE IN WATER.

In order to have the results on the barley and on the malt comparable, the percentage results obtained on the malt are reconverted to the equivalent weight of its original barley. To do this it is necessary to know the weight of 1,000 kernels of dry barley and of 1,000 kernels of dry malt. This weight of dry barley being expressed by Wb and of dry malt by Wm, any percentage weight of a constituent in the dry malt is converted back to its original barley value by multiplying by the factor $\frac{Wm}{Wb}$.

It was found that the relation of the weight of the grain to that of the extraction water was a very important factor, owing to the different solubility of globulins in salt solutions of varying strength, and in order to make this relation constant the following conditions were established:

The weight of barley and of malt taken was such that when the solution was made to its final volume it contained the extract and insoluble portions of amounts corresponding exactly to 20 grams of dry barley in 100 cc. For the extraction 75 per cent of the required amount of water was taken at first, the mixture shaken in a revolving shaker for a definite time, the flask then filled to the required volume, and after thorough mixing allowed to stand for six hours, measuring the time from the beginning of the shaking. It was found that six hours extracting removed all of the nitrogenous substances soluble in cold water and that any decided increase in the length of time of extraction was liable to introduce errors due to the action of proteolytic enzymes.

In order to obtain, by calculation, the amount of malt, which in the final volume of the mixture of malt and water shall contain in 100 cc the exact equivalent of 20 grams of dry barley, the moisture content of both barley and malt must be known; also the relation of the dry weight of 1,000 kernels of barley to that of the resulting malt. Knowing these factors, the following general formula is obtained:

$$\frac{Wm.\,C.\,V}{Wb\,(100-Mm)}=X,$$

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[a] Transactions of the Guinness Research Laboratory, 1903, vol. 1, pt. 1, p. 61.

in which X=weight of air-dry malt to be taken; Wm=weight of 1,000 kernels of dry malt; Wb=weight of 1,000 kernels of dry barley; Mm=percentage of moisture in air-dry malt; C=required concentration in terms of grams of dry barley per 100 cc of the final mixture; V=volume of final mixture in cubic centimeters.

After the extraction is completed the contents of the flask are filtered and definite volumes (100 cc) of the clear filtrate taken. In one of these portions the amount of nitrogen is determined by the Kjeldahl method. This represents the total soluble nitrogenous compounds. The other portion of the filtrate is boiled down to small bulk in a beaker, again made up to its original volume, and filtered. The nitrogen in this filtrate represents the soluble nitrogenous compounds not coagulable by boiling, and the difference between this and the total nitrogen is the nitrogen representing the nitrogenous substances coagulable by boiling.

NOTES ON THE DETERMINATION OF ALBUMINOID NITROGEN IN CEREALS.

By J. A. Le Clerc and W. C. Lounsbury.

In 1880 Stutzer [a] recommended the determination of albuminoid nitrogen by means of copper hydroxid. With substances rich in leucin and solanin or tannic acid alkaloids, a previous treatment with a weak acetic acid alcohol solution was necessary.

Many substances rich in protein—e. g. cotton-seed oil cake, linseed oil cake, soy bean, etc.—when boiled and treated with copper hydroxid filter very slowly, the filtrate being turbid and the results not always concordant. The incomplete precipitation of proteid substances which are rich in alkali phosphates is due probably, as Schulze suggested, to the action of the copper hydroxid on the alkaline phosphate, which forms some copper phosphate and free alkali. This may be prevented by previous treatment with the acetic acid alcohol solution.

In 1886 Stutzer [b] recommended the addition of several cubic centimeters of concentrated alum solution to oil cakes, seeds, etc., which are rich in alkaline phosphates, before adding the copper hydroxid and boiling, or, in case of substances rich in starch, heating in a water bath for ten minutes. The alum causes a decomposition of the alkaline phosphate into insoluble alum phosphate and potassium sulphate, while without alum, in the presence of copper hydroxid, there would be formed copper phosphate and free alkali or an alkali-reacting potassium phosphate, which in consequence of the alkalinity prevents the complete precipitation of the albuminoids by copper hydroxid, as proteids are precipitated only in neutral or slightly acid solutions.

In making many determinations of albuminoid nitrogen by the Stutzer method, it was noticed that the results obtained with and without the addition of alum were not at all concordant, i. e., the per cent of albuminoid nitrogen with the use of alum was from 0.10 to 0.20 per cent lower than when no alum was used. That this lower result when alum is used is due to the dissolving action of the alum on the albuminoids is amply shown when the gluten itself is treated. Extracting 0.2 gram of gluten with 100 cc of water and determining the albuminoid nitrogen in the residue after treatment with the various reagents mentioned, the following results were obtained:

	Albuminoid nitrogen, per cent.
Gluten alone	13.05
Gluten after extraction with water	12.63
Copper hydroxid	13.12
3 cc of alum	12.28
3 cc of alum and copper hydroxid	12.84

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[a] J. Landw., 1880, *28:* 103.

[b] J. Landw., 1886, *34:* 151.

The results obtained on 1 gram of oats after extraction with 100 cc of water and the addition of varying amounts of alum and normal amount of copper hydroxid show a continual increase in the amount of amido bodies:

	Per cent.
Total nitrogen	1.99

	Albuminoid nitrogen, per cent.
With copper hydroxid	1.93
3 cc of alum+copper hydroxid	1.85
5 cc of alum+copper hydroxid	1.82
10 cc of alum+copper hydroxid	1.78
15 cc of alum+copper hydroxid	1.75
20 cc of alum+copper hydroxid	1.70

However, if instead of alum, alumina cream be used, or if a larger amount of copper hydroxid be added, the results are then more nearly equal to those obtained by the use of copper hydroxid alone.

Although the difference in results between the addition of 3 and 5 cc is very slight, yet the fact, as shown above, that the more alum used the more amido bodies are found makes the method unsatisfactory.

When the very small amount of amids present in cereals is considered, and when such investigations as von Strusiewicz[a] recently published show that the food value of amido bodies is practically equal to that of albuminoids, then the question arises, Of what importance is the albuminoid determination?

Whether the results obtained by von Strusiewicz shall stand, and it will be necessary to determine the total nitrogen only or whether further investigations will refute those results, further experiments will prove. In the meantime, the method for the determination of albuminoids in cereals, at least, will be more nearly correct if the alum be omitted, as our results show that alum causes some of the original proteids to go into solution, and only when twice the amount of copper hydroxid is added is a complete precipitation of the albuminoids possible.

The authors are indebted to Mr. T. C. Trescot for making the nitrogen determinations necessary in this study.

REPORT OF COMMITTEE A ON RECOMMENDATIONS OF REFEREES.

By John P. Street, *Chairman.*

(Phosphoric acid, potash, nitrogen, soils, ash, and insecticides.)

(1) Potash.

It is recommended—

1. That the study of the volumetric method be continued, with particular attention to its use in soil analysis.

Adopted.

2. That a method of incineration at low temperature and subsequent solution in dilute acid be examined [for the determination of organic potash in mixed fertilizers] and reported on at the next annual meeting.

Adopted.

3. (The association was asked to consider carefully the adoption as official of the following two methods coming over from the preceding year for final consideration, the referee for 1905 not giving these changes an unqualified indorsement):

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[a] Zts. Biol., 1905, *47:* 143.

(1) That the directions for making the solution in mixed fertilizers given under the determination of potash in Bulletin 46, page 21, be made to read as follows:

> Boil 10 grams of the sample with 300 cc of water plus 5 cc of hydrochloric acid for thirty minutes. Add a few drops of phenolphthalein and carefully neutralize with sodium hydrate free from potash, avoiding a large excess. Add sufficient powdered ammonium oxalate to precipitate all the lime present, cool, dilute to 500 cc, mix, and pass through a dry filter.

This recommendation received only a qualified indorsement by the referee for 1905 (see p. 138), and after some discussion by Messrs. Frear, Carpenter, Hartwell, and Wiley, the vote was taken in which only chemists in charge of fertilizer control were qualified to participate, the vote resulting in the loss of the motion. It seemed to be the opinion of the majority that the time was not ripe for the adoption of a change, although some modification of the method might be desirable.

(2) That the directions for the determination of moisture in potash salts, sodium nitrate, and sulphate of ammonia, given under the determination of moisture, Bulletin 46, page 11, be made to read as follows:

> In potash salts, sodium nitrate, and ammonium sulphate heat 2 grams at 130° in oil oven for 10 hours. The loss in weight is considered as moisture.

The motion to make this charge official was lost:

(2) Phosphoric Acid.

It is recommended—

1. That the referee on phosphoric acid take up, for report at the next meeting of the association, methods applicable under American conditions to the official examination of basic slag phosphates. (Motion by Mr. Frear referred to committee.)

Adopted.

2. That the subject of an accurate determination of iron oxid and alumina in rock phosphates be examined by the referee on phosphoric acid and an official method be recommended to the association next year. (Motion by T. S. Gladding referred to the committee.)

Adopted.

3. That a number of chemists be requested to send to the referee on phosphoric acid samples of the citrate ammonia solution employed by them, and that the referee examine such samples as to neutrality and that such examination be reported to the chemists at the next annual meeting. (Motion by T. S. Gladding referred to the committee.)

Adopted.

(3) Nitrogen.

It is recommended—

1. That the study of availability by both the neutral and the alkaline permanganate methods be continued, particularly with the view to determining the amount of material to be used in the neutral method on commercial fertilizers. (Continued from 1905.)

Adopted.

2. That in the official Gunning method for the determination of nitrogen the addition of one-half to three-quarters of a gram of copper sulphate, after digesting with sulphuric acid and potassium sulphate for one-half hour, be studied by the referee. (Recommendation by F. D. Fuller referred, on motion, to the committee.)

Adopted.

3. At the close of the report of Committee A, Mr. Davidson made the following motion, which, as it involved a change in an official method, was referred to the referee on nitrogen for recommendation in 1906. The motion is as follows:

Recommendation for Standardizing the Hydrochloric Acid Solution.

It is recommended—

That the silver precipitation method (Bul. 46, Rev., p. 14), under "4. Determination of nitrogen," be changed to read as follows:

> By means of a preliminary test with silver nitrate solution, to be measured from a burette, with excess of calcium carbonate to neutralize free acid and potassium chromate as indi-

cator, determine exactly the amount of nitrate required to precipitate all the hydrochloric acid. To a measured and also weighed portion of the standard acid add from a burette one drop more of silver-nitrate solution than is required to precipitate the hydrochloric acid. Heat to boiling, cover from the light, and allow to stand until the precipitate is granular. Then wash with hot water through a Gooch crucible, testing the filtrate to prove excess of silver nitrate. Dry the silver chlorid at 140° to 150° C.

(4) INSECTICIDES.

Three methods coming up for final action as to their adoption as official methods were first considered.

It is recommended—

1. That Methods I and IV of the four modifications of the Avery-Beans method of determining total arsenic in Paris green[a] be adopted as optional official methods.

Adopted as official.

2. * * * and that the thiosulphate method be adopted as an optional method using N/20 instead of N/10 thiosulphate solution.

Adopted as official.

3. That the Blank and Finkenbiener peroxid method be adopted as the official method of determining formaldehyde in strong solutions, and that the Romijn potassium cyanid method be adopted as an official method for analyzing dilute solutions.

Opposed by referee for 1905 and motion lost.

4. That the work on London purple be continued, special attention being given to the modifications proposed by Mr. Davidson for the removal of part of the color. (See p. —.)

Adopted.

5. That the hydrogen peroxid method for determining sulphur in sulphur dips and similar compounds be further tested, effort being made to have all analyses made simultaneously.

Adopted.

6. That the hydrogen peroxid method for determining formaldehyde be tested in its modified form.

Adopted.

7. That the methods of determining available chlorin in bleaching powder be further compared.

Adopted.

(5) SOILS.

It is recommended—

1. That the determination of water-soluble plant food contained in the soil be further investigated.

Adopted.

2. That further study be made of the use of fifth-normal nitric acid in the determination of available plant food.

Adopted.

3. That the use of ammonium sulphate for the removal of the last appreciable amounts of barium from the solution of total alkalies be thoroughly tested with a view to its incorporation in the official methods.

Adopted.

4. That the sodium peroxid method for ultimate analysis and the preliminary separation of phosphorus as iron phosphate in ammoniacal solution previous to its re-solution and precipitation as ammonium phosphomolybdate be further investigated.

Adopted.

(Recommendations 5 and 6 were made as the result of the following resolution offered by Mr. Davidson and referred to the committee:

Resolved, That Committee A on recommendations be requested to consider the question of size of mesh of sieve to be used in preparing samples of soil for analysis.)

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 90, pp. 96–97.

5. That the third line, fourth paragraph, section 1, under "VI. Methods for the analysis of soils" (Bul. 46, p. 71), be changed to read "one millimeter," instead of "one-half millimeter," and that the referee be requested to consider this matter in his work with the view to its adoption next year.

Referred to referee for 1906 for recommendation as to final action.

6. That on page 74, section *h*, first line (Bul. 46), the clause "passed through a sieve of 1 millimeter mesh" be omitted.

Referred to referee for 1906 for recommendation as to final action.

(6) ASH.

It is recommended—

1. That the provisional nitric-acid method for sulphur in plants be dropped.

Adopted.

2. That the peroxid method be adopted as a provisional method for sulphur in plants as follows:

Weigh out 15 grams of sodium peroxid (free from sulphates) and introduce about three-fourths of it at once into a 100 cc nickel crucible; add a little water and boil over a sulphur-free flame until excess of water is completely driven off. Allow to cool until pasty and stir 2 grams of material into it as quickly as possible; heat cautiously until danger of foaming has passed, adding the remainder of the peroxid in small portions from time to time to complete the oxidation. After fusion is complete, allow crucible to cool; dissolve contents in water, transfer to a beaker, and add a slight excess of hydrochloric acid. Heat to boiling, filter if not perfectly clear; dilute to about 400 cc and add 10 cc of a 10 per cent solution of barium chlorid. Let stand over night, filter, and weigh the barium sulphate in the usual manner. Make blank test with the reagents.

Adopted.

3. That the referee for next year be requested to investigate the Barlow-Tollens method as a means of distinguishing between organic sulphur and sulphur of the ash.

Adopted.

(7) SEPARATION OF NITROGENOUS BODIES.

A. MILK AND CHEESE PROTEIDS.

It is recommended—

1. That this work be continued, and that special attention be given to the problem of making a complete extraction of water-soluble nitrogenous bodies and to the complete separation of these in filtering.

Adopted.

2. That the amount of water used in making the extract be increased from 500 cc to 1,000 cc.

Adopted.

3. That after the fat and insoluble nitrogenous bodies have been removed by the absorbent cotton, the filtrate be passed through asbestos.

Adopted.

B. SEPARATION OF VEGETABLE PROTEIDS.

It is recommended—

That the method of Horace T. Brown (Transactions of Guinness Research Laboratory, vol. 1, part 1, p. 61, 1903), on the Estimation in Barley and Malt of the Total Amount of Nitrogenous Substances Soluble in Water, be used for the separation of nitrogenous bodies in barley and malt. (See page 149.)

Adopted as a provisional method.

C. SEPARATION OF MEAT PROTEIDS.

No recommendations reported to committee.

Doctor Wiley, calling attention to the fact that a majority of the States require that the potash in fertilizers shall be water soluble, stated that he deemed it unwise to insert methods of analysis in laws; that the law should be broad and general, leaving the determination of methods of analysis to scientific bodies, and urged that all members of the association, when consulted in regard to fertilizer legislation, should advise such action in framing State laws.

ADDRESS OF THE ASSISTANT SECRETARY OF AGRICULTURE.

The Assistant Secretary of Agriculture, Hon. W. M. Hays, addressed the association briefly, as follows:

Gentlemen of the Association: I wish to greet you and to say that I am most thoroughly in sympathy with all your work. This organization has a peculiar standing as a scientific body on account of its intimate relations to the industrial and economic interests of the country. I have some acquaintance with the pure-food work that some of your members are doing, especially in Minnesota, North Dakota, and Pennsylvania, and I am more and more convinced that, with the scientific basis afforded by this association and the close relations with the people established by your members in their several States, you are gaining a powerful hold on this question of pure food, and that the issue is going to be supported by the people and the necessary legislation obtained to secure for the American people such trade conditions as will insure the pure food that modern methods and modern times demand. Your work on fertilizers, cattle foods, etc., also is of great interest.

REPORT OF COMMITTEE B ON RECOMMENDATIONS OF REFEREES.

By L. L. Van Slyke, *Chairman.*

(Dairy products, foods and feeding stuffs, sugar, tannin, and drugs.)

(1) Sugar.

A. CHEMICAL METHODS OF SUGAR ANALYSIS.

It is recommended—

1. That the work as outlined in the report of the referee on sugars be continued until uniform methods are obtained for the various reducing sugars; that copper-sugar factors be determined for the various concentrations of the different reducing sugars and for various mixtures and proportions of sucrose and the reducing sugars.

Adopted.

2. That the methods selected by the international committee for unifying methods of sugar analysis, now provisional, be made official. (See Proceedings, 1902, pp. 58, 59, pars. 1 to 9, inclusive.)

Goes over for action in 1906.

3. That method (*a*) for the determination of copper in the cuprous oxid precipitate, requiring reduction in hydrogen (see Bul. 46, p. 37), be dropped as an official method of this association.

Goes over for action in 1906.

4. That methods (*c*) and (*d*) for the determination of copper in the cuprous oxid precipitate, requiring the electric deposition of the metal (see Bul. 46, p. 38), be dropped as official methods of this association.

Goes over for action in 1906.

5. That Low's thiosulphate method for determining the copper in the cuprous oxid precipitate be substituted for the volumetric permanganate method as a provisional method. (See Bul. 46, p. 38.)

Action deferred until 1906 by request of referee.

B. SPECIAL ANALYTICAL METHODS OF SUGAR ANALYSIS.

It is recommended—

1. That the work upon the separation of sugars next year be submitted to collaborative trial.

Adopted.

2. That the work upon the identification and determination of the various organic solids not sugar be continued.

Adopted.

C. MOLASSES ANALYSIS.

See p. 24, report of associate referee, for full text of recommendations.

Recommendations 1 to 5 go over to 1906 for recommendation by referee and final action.

Recommendation 6 was adopted.

(2) Foods and Feeding Stuffs.

The following recommendations were made by C. A. Browne, jr., associate referee on sugar, who says: "The extent to which this class of feeds is at present being adulterated renders an action of this character exceedingly desirable."

It is recommended—

1. That a committee be appointed by the association for the establishment of a set of standards for the composition of the various unmixed feeds—such as wheat bran, rice bran, cotton-seed meal, etc.—these standards to give the maximum or minimum percentages of protein, ash, fat, and crude fiber which these different unadulterated feeds should contain.

Referred to the food standards committee.

2. That the method adopted by the Fifth International Congress of Applied Chemistry[a] for the analysis of molasses feeds be adopted by the association. The method reads as follows:

> Twenty-five grams of the molasses feed are dried for three hours at 80° C.; after cooling the loss in moisture is determined and the residue thoroughly ground. Five grams of the powdered feed are then freed from sugars by washing upon a filter paper or Gooch crucible with 100 cc of cold water, added drop by drop. The residue is then dried in a water oven and extracted with ether in the usual way.

Argument for recommendations.—The present official method for fat determination is not applicable to the molasses feeds, owing to the occlusion of fat by the dried residue of sugars. Our work at Audubon Park upon molasses feeds, which are very extensively manufactured and used in Louisiana, has demonstrated this fact conclusively. Although the constitution states (Article VII) that no changes shall be made in our official methods of analysis except by unanimous consent until the association has thoroughly tested such proposed change, I believe that the circumstances of the case, supported as they are by the authority of the international commission, should lead to the immediate adoption of this resolution.

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[a] Bericht über die Arbeiten der Internationalen Kommission für die Analyse der Kunstdünger und Futtermittel, p. 27.

Referred to referee for recommendation in 1906 as to final action.

(3) DAIRY PRODUCTS.

It is recommended that the referee for next year be requested—

1. To continue the study of the preservation of milk samples intended for the future determination of milk proteids, and the suggestion is made that some special treatment of the preserved samples, previous to analysis, may be found useful in bringing the proteids back into such condition that they may be accurately determined by the usual methods of analysis.

Adopted.

2. To study methods for determining sugars in condensed milks and dried milks or milk powders.

Adopted.

3. To study methods of detecting the adulteration of butter with small quantities of foreign fats.

Adopted.

(4) TESTING OF CHEMICAL REAGENTS.[a]

The amount of information at present possessed by the committee is insufficient to warrant recommending any action relative to the adoption of standards for the chemicals so far investigated, but the committee does not recommend that the work be continued and that the work of the succeeding committee be extended to include ten additional chemicals which in the opinion of the committee may be considered the most important.

Adopted.

(5) MEDICINAL PLANTS AND DRUGS (OPIUM ASSAYING).

It is recommended—

1. That this association adopt the method prescribed by the eighth revision of the United States Pharmacopœia, page 329, as a provisional method for gum opium, powdered opium, deodorized opium, and granulated opium.

2. That the work on the assay of opium be continued, utilizing such methods as appear to give satisfactory results, and that the work be extended to ipecac and golden seal.

Adopted.

3. That associate referees be appointed to take up different features of the work.

Adopted.

(6) TANNIN.

It is recommended that the following questions be made subjects of collaborative research during the ensuing year:

1. Soluble solids filtration, with especial reference to the time-contact method, so termed, in conjunction with the temperature problem.
2. Analysis of liquors and the effect of the acidity of liquors upon the analysis.
3. Estimation of acid in tan liquors, with a view to improving the present method.
4. The influence of acidity and alkalinity upon the chroming of hide powder and upon the subsequent analysis. The elimination of the sulphate factor and the merits of a fully or partially chromed, prepared hide powder.
5. Extraction, for the purpose of confirming or rejecting the recommendations of the referee.
6. The Parker-Payne method of tannin analysis.
7. Estimation of nitrogen in leather and tan liquors.

Adopted.

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[a] Referred by error to this committee, together with recommendations on drugs, and acted on by the association at this time.

It is further recommended that the following methods and processes be adopted provisionally:

8. The chroming of hide powder by the addition of the entire amount of chrome alum at one time.

9. Limiting the moisture content of wet chromed hide powder used for analysis between 70 and 75 per cent.

10. The analysis of liquors as recommended by the referee.

11. The form of apparatus known as the combined evaporator and drier.

Adopted.

Finally, it is recommended that—

12. An official method be drawn up from the present method (Circular 10, revised, 1902), including the provisional methods recommended in this year's report. (Draft of such a method submitted with report.)

Action deferred to 1906.

At the close of the report of Committee B, the secretary presented a letter from a committee of the American Leather Chemists' Association, signed by W. H. Teas, H. C. Reed, and J. H. Yocum, making the following suggestions in regard to the relations existing between the two associations in regard to the tannin work. These suggestions were in brief as follows:

1. That the executive committee of the Association of Official Agricultural Chemists appoint a special committee on recommendations for the tannin section and that the association appoint the same referee and associate referee on tannin as are appointed by the American Leather Chemists' Association.

2. That the Association of Official Agricultural Chemists abandon the appointment of a referee and associate referee on tannin and consequently omit for the present any supervision of the tannin methods.

By motion the suggestions made in this letter were referred to the referee for 1906 for consideration.

The association adopted a resolution of thanks to the George Washington University; to the Hon. James Wilson, Secretary of Agriculture; to the Hon. Willet M. Hays, Assistant Secretary of Agriculture, and to the president and the secretary of the association.

REPORT OF THE COMMITTEE ON FOOD STANDARDS.

By William Frear, *Chairman.*

On behalf of the committee on food standards, I beg to submit the following report of progress covering the period since the last meeting of this association. During this period the committee has held two meetings; one in Washington from December 12 to 20, inclusive, 1904; a second in Chicago, May 29 to June 5, 1905.

At the former meeting the committee adopted for final recommendation standards for grains, meals, refiner's sirup, honey, wine, and vinegar, after carefully considering the extensive correspondence called forth by the publication of the tentative standards for these schedules and weighing the facts developed at the hearings given by the committee to various trade representatives at the meeting of May, 1904, in New York. Upon further consideration of the question of form, in the light of various suggestions and criticisms, it was decided to rephrase the standards proclaimed November 21, 1903, so that the chemical limits should be more intimately connected with that portion of each standard previously known as the "definition." The standards recommended in 1903 and 1904 were proclaimed by the Secretary of Agriculture, December 20, 1904, and subsequently published as "Circular No. 13, Office of the Secretary, United States Department of Agriculture." During the December meeting the committee also formulated tentative standards for fruit and fruit products, flavoring extracts, edible vegetable oils, and salt, partly upon the basis of proposals by G. E. Colby, California, for edible vegetable oils, and

F. W. Woll, Wisconsin, for table and dairy salts, and partly on the basis of preliminary work accomplished by several members of the committee. The tentative standards thus prepared were revised by correspondence and published for criticism March 31, 1905.

At the Chicago meeting the time was largely devoted to hearings upon matters relating to the schedules of tentative standards just published. Among those who appeared to discuss the standards for fruit and fruit products were Col. Philo Hersey, of San Jose, Cal., representing the chamber of commerce of San Francisco and other similar California organizations, who suggested amendments to the standards for dried fruits; representatives of the Association of Manufacturers and Distributors of Food Products, who urged the desirability of widening the standards so as to permit the use of glucose in fruit preserves, jams, etc. Representatives of a number of large wholesale houses, and also of the Corn Products Company and other glucose manufacturing companies, strongly supported this plea. The executive committee of the National Association of Packers of Pure Food Products, Mr. Willard G. Rouse, president, acting as spokesman, welcomed the movement for uniform standards for food products, urged the desirability of early action with respect to standards for canned vegetables, and expressed themselves as prepared to conform strictly to the standards that shall be adopted. It was also noted that in connection with standards for canned fruits and canned vegetables some specification should be included with respect to the containers, so as to diminish the present tendency to the use of tin cans with an inferior coating.

Upon the subject of flavoring extracts the committee was greatly assisted by the advice of Dr. Edward Kremers, dean of the School of Pharmacy of the University of Wisconsin, whose exceptional experience upon the subject of essential oils enabled him to communicate many facts of value respecting the raw materials used in the manufacture of extracts. The committee is also indebted to Doctor Halberg, of the committee on revision of the United States Pharmacopœia, for many excellent suggestions. The representatives of the extract trade strongly urged the admission of the so-called "terpeneless" extracts of lemon and orange and of extracts of cinnamon, wintergreen, etc., weaker than the corresponding pharmacopœial spirits. In addition to the hearings upon these subjects, representatives of a number of the larger milk-condensing companies of America were afforded an opportunity to present an argument for the reopening of the standards for condensed milk, and particularly for the variety of condensed milk hitherto appearing upon the market under the name "evaporated cream;" but after a very careful consideration of the facts presented by these gentlemen, representing the various interests concerned, the committee concluded that it was not desirable to reopen the consideration of these standards at this time.

In view of the concern expressed by the many producers of honey, lest the standard for this product proclaimed December 20, 1904, might lead to the condemnation of honeys containing small amounts of honeydew, which apiculturists claim they are unable to exclude, the committee adopted the following resolution:

> The standard does not in any way exclude small quantities of honeydew from honey. We realize that bees often gather small quantities of honeydew that can not be detected in the finished product by chemical means and does not damage its quality. It is only when relatively large amounts are gathered that the quality of the honey is impaired, and it fails to meet the requirements of the standard. It is generally agreed that such a large amount of honeydew is injurious to the quality of the product, which can not then be properly regarded as honey.

At the conclusion of the hearings the committee provisionally modified the tentative standards for fruit products so as to make a separate class of standards for preserves, jams, and fruit butters into the composition of which glucose enters. Some discussion having arisen as to the number of chemical characteristics for which limits should be expressed in the case of edible vegetable oils, it was decided to request from the various members of the association and others interested in the subject an expression of their individual experience and judgment upon the question. We regret, however, to say that the response to the request has been meager. With respect to flavoring extracts, it was decided to adopt provisionally such amendments of the schedule as should provide for the retention of the pharmacopœial standards for preparations sold under pharmacopœial names, but should fix lower standards for certain of the extracts in cases where the pharmacopœial preparations had been given a high concentration with a view to use as stomachics or as a means of masking the disagreeable flavors of certain medicines. Separate standards for "terpeneless" extracts of lemon and orange, for tonka extract, and the mixed "vanilla and tonka extract" also were provisionally adopted.

The revision of these tentative schedules has been completed by correspondence since the Chicago meeting, and the revised schedules have recently been distributed to the members of the association and to the various trade interests concerned for further criticism.

The committee desires to express its appreciation of the great assistance rendered to it by many of the members and the cordial spirit of cooperation shown by influential representatives of the various manufacturing and chemical interests concerned.

REPORT OF COMMITTEE ON FERTILIZER LEGISLATION.

By H. W. Wiley, *Chairman.*

During the past year the committee has by correspondence and otherwise made considerable progress in the duties assigned to it. The opinion of the various members of the committee has been obtained respecting the form which National legislation should take in case it is finally deemed advisable to present a bill to Congress.

We have also consulted with representative manufacturing firms regarding Federal legislation. As a result of these conferences a wide divergence of opinion appears, both with respect to the desirability of such legislation and as to its form. The committee is therefore of the opinion that it is advisable before going further to secure a full and free expression from the officials of the various States charged with the inspection of fertilizers regarding the desirability of National legislation and the character of the bill embodying it.

The committee is also of the opinion that a similar opportunity should be given to the fertilizer manufacturing associations and individual firms and that the leading agricultural organizations of the country representing the farmers be consulted.

We therefore recommend that the committee be continued, with instructions to consult the various interests mentioned above, to digest and tabulate the data obtained, and to report at the next meeting whether it is deemed desirable to attempt to secure National legislation regulating interstate commerce in fertilizers and fertilizing materials or whether the committee should be discharged from further consideration of the subject.

Mr. Rose submitted the following paper, requesting an expression of opinion on the points enumerated. The paper was referred to the committee on fertilizer legislation for consideration.

WHAT VARIATIONS FROM MAXIMUM GUARANTEED ANALYSIS OF FERTILIZERS AND FEED STUFFS SHALL BE CONSIDERED ADULTERATIONS OR DEFICIENCIES?

By R. E. Rose.

Probably no decisions are so frequently demanded of the officers charged with the execution of the various fertilizer and feed laws of the different States as those arising from the deficiency of valuable ingredients in one case and the excess of others found in fertilizers and feeds. The guarantee, honestly made, shows certain percentages of valuable material. The analysis often shows a deficiency in one or more ingredients guaranteed—generally the most costly—and an excess of others—frequently the least valuable. The problem is, To what extent shall these variations be allowed? Shall the excess in one ingredient be allowed to offset the deficiencies in another? From a strictly chemical viewpoint this question is of course not debatable; the material should contain not less than the guaranteed amount of each ingredient. However, practically, except where large allowances are made and correspondingly low percentages of each ingredient are guaranteed, variations are often found, particularly where the materials used are coarse and carelessly mixed or are of such different specific gravity, when mixed dry, as to allow a separation of the various ingredients in the mixing or in transit.

It is not unusual—in fact, in many instances it is the practice—to mix fertilizers and stock feeds in ton lots, using the proper amounts of the various materials to justify the guarantee or formula, the manufacturer honestly placing in each ton the necessary material to meet his guarantee, with usually a slight excess of each valuable ingredient. Because of hasty or careless mixing the blending is not perfect; a sample drawn from the lot will not be representative of the totals of the ingredients used. A deficiency of one ingredient—probably nitrogen—will be found, with an excess of another—generally phosphoric acid. Another sample from the same lot will often show contrary results. Shall the manufacturer be allowed credit for the excess to offset the deficiency, allowing that the "commercial value" of the one would balance the other?

This problem is frequently presented to the executive officer. Some rule of action, some general provision, in such cases should be provided.

In the "Cotton States"—the largest consumers of commercial fertilizers—it is frequently found that nitrogen or potash is more or less deficient. In nearly every case of deficiency in nitrogen or potash, or both, an excess of phosphoric acid is found, frequently equalling or exceeding in "commercial value" the deficiency. Shall the material be penalized as fraudulent or deficient? If not, what general rule should be adopted to govern in such cases, the honesty of the guarantee being assumed?

This question is also applicable to stock feeds. Shall a deficiency in "protein," "digestible carbohydrates," or "fat" be balanced by an excess in one or both exceeding the others? If so, what percentage of deficiency may be allowed? In other words, where shall the line be drawn between legitimate goods and fraudulent or deficient goods? Shall a fixed standard be established, beyond which variations shall not be allowed?

Another matter of general importance in the practical operation of fertilizer and feed laws is a uniform allowance of differences between analysts in analyzing the same sample. What may be considered the maximum allowable variation of results? Ordinarily "twenty points" (0.20) is allowed between chemists. This, however, is rather a broad allowance in small percentages; it frequently amounts to 20 per cent of the total found, particularly in mixtures low in potash or nitrogen. Some definite rule is needed to determine when a third or check analysis is necessary, in order that a fair determination be had and equal justice given the manufacturer and consumer.

REPORT ON MEDICINAL PLANTS AND DRUGS.

By L. F. Kebler, *Referee.*

Since the last meeting of the association no important contributions have appeared in current literature bearing directly on the assaying of opium, with the exception of an article by E. Mallinckrodt and E. A. Dunlap.[a] This is a very interesting contribution in that it clearly points out at least one of the agents which materially contaminate the final morphine obtained in the assay of opium.

Many observers have undoubtedly noticed the crust and scale formation in precipitating morphine in the regular course of assay, and many have also observed that the amount of impurity associated with the morphine is frequently increased by the length of time permitted for the precipitation or crystallization of the morphine. It has also been observed that there is present some agent in the precipitated morphine which neutralizes acids in the same manner that morphine itself does, but exactly what this substance was has only been conjectured. The above authors have clearly shown that one of the agents which cause the disturbances referred to is calcium ammonium meconate.

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[a] J. Amer. Chem. Soc., 1895, *27:* 946.

During the past year the eighth revision of the United States Pharmacopœia made its appearance and went into effect September 1, 1905. While the method adopted in the Pharmacopœia is not new, being simply a slight modification of the Squibb method, it differs from the 1890 pharmacopœial method in that the morphine is purified with lime water. The particular interest connected with the 1900 method for assaying opium and its preparations is the fact that many of the State laws recognize the United States Pharmacopœia as the standard for all preparations recognized by it, and undoubtedly chemists will be called on more frequently to test chemicals and medicinal agents during the life of the present revision of the Pharmacopœia than during corresponding periods of former editions.

During the past year the work on medicinal agents was again confined to the methods for determining morphine in opium. Outlines of several methods were sent to about 40 different pharmaceutical chemists, with 10 favorable responses. Completed and partial results were sent in by 9 workers. All calculations and solutions were directed to be based on the data contained in the eighth revision of the United States Pharmacopœia. The directions sent out were as follows:

POWDERED OPIUM.

Method 1.—United States Pharmacopœia, Eighth Revision, page 329, with additions.

Run two sets of duplicates on opium as received and report results for each set.

(1) Weigh the crystals in the inner filter counterpoised by the outer filter.

(2) Remove morphine crystals from filter paper, weigh on tared watch glass.

Mix the morphine of the two sets, powder same, test portions of the mixture by the following methods, and report per cent of purity.

(3) Purity by lime-water method, United States Pharmacopœia, eighth revision, using 0.5 gram of morphine.

(4) Place 0.5 gram of morphine into a 120 cc Erlenmeyer flask, add 35 cc each of N/10 potassium hydroxid and distilled water, agitate the contents of flask by a rotary motion at frequent intervals during half an hour, and proceed from this point as directed by the Pharmacopœia in determining purity of morphine by lime water.

(5) To 0.5 gram of morphine add 18 cc of decinormal sulphuric acid, warm slightly to bring about a complete combination of the alkaloid and acid, add 50 cc of distilled water and 5 drops of cochineal solution. Then titrate back the excess of acid with N/40 potassium hydroxid solution. Each cubic centimeter of decinormal sulphuric acid solution represents 30.09 mg of crystallized morphine.

(6) Determine per cent of inorganic matter in powdered morphine and report results.

Method II.—United States Pharmacopœia, eighth revision, modified by Lamar.

Proceed as directed by the Pharmacopœia to precipitation of morphine. To the 20 grams of aqueous extract add 60 grams of alcohol, cork flask, shake well for one minute, and set aside for thirty minutes, during which time the precipitated material should have completely subsided. Decant the clear supernatant liquid into a tared 250 cc evaporating dish, transfer the precipitate to a 7 centimeter filter previously moistened with a mixture of alcohol (three parts) and water (one part). The last portions of the residue are transferred to the filter by using small portions of the above hydro-alcoholic solution. The filtrate is to be collected in the tared evaporating dish. Continue washing the residue and filter by dropping the alcoholic solution on the filter and the residue until the filtrate is no longer bitter. Add 35 cc of water to the contents of the evaporating dish and evaporate on water bath to 14 grams, then proceed as directed by the Pharmacopœia.

Procure the same data for the morphine thus obtained as outlined under Method I.

Method III.—United States Pharmacopœia, eighth revision, modified by Dohme.

Place 10 grams of the opium in a flask provided with a condensing tube and heat with 50 cc of 75 per cent alcohol for about ten minutes. Decant the fluid through a filter into a porcelain dish and extract the opium once more with 50 cc of the same alcohol. Filter, put filter back in the flask, heat the contents of the flask with 30 cc of the alcohol, filter again, and wash filter and residue with about 20 cc of the alcohol.

The combined alcoholic solutions are evaporated to a thin syrup, and then water is added until no more resin is precipitated. The aqueous fluid is filtered and after thorough washing evaporated to about 15 grams.

Then proceed as given under opium in the United States Pharmacopœia, 1900.

Procure the same data for the morphine obtained as outlined under Method I.

Method IV.—Stevens's, with additions.

Run two sets of duplicates.

Place 8 grams of opium in a 120 cc Erlenmeyer flask with 4 grams of fresh quicklime (not air slacked) and 20 cc of water, then agitate and stir with a glass rod until a uniform mixture results. Add 38 cc of water and stir frequently during one-half hour. Filter through a dry filter 10 centimeters in diameter and transfer exactly 30 cc to a 120 cc flask, add 8 cc of alcohol and 20 cc of ether, mix well, then add one gram of ammonium chlorid, shake the mixture well and frequently during half an hour, then set aside, in a cool place, for twelve hours.

Collect the morphine of one set of duplicates on counterpoised filter papers and the other set on a pledget of absorbent cotton, lodged in the throat of a funnel (both being dried to a known, constant weight) in the following manner: Remove the stopple carefully and transfer any adhering morphine to the flask. Pour the ethereal layer on the cotton or filter paper, as the case may be, wash the contents of the flask with 20 cc more of ether, transfer to respective funnels, and, when this ether has passed through, pour the contents of the flask into the funnels. Remove the remaining adhering crystals to the proper funnels by means of small portions of morphinated water and wash the contents of the funnels with morphinated alcohol until the filtrate passes colorless. When the crystals have drained, dry to constant weight at about 60° C. Determine the weight of the morphine on the filter paper and cotton, respectively, and report results.

Remove morphine from filter paper, powder, determine purity of same by Method I, parts 3 and 4, using about one-half of the morphine for each operation.

Determine purity of morphine on cotton by treating with decinormal sulphuric acid as follows: Remove cotton and crystals from funnel by means of a small glass rod, drawn out to a curved point, to a beaker, rinse the crystals adhering to the funnel into the same beaker with 24 cc of decinormal sulphuric acid and 25 cc of distilled water, the latter following the former. Agitate the contents of the beaker until the crystals are dissolved and titrate back the excess of acid with N/40 potassium hydroxid, using cochineal as indicator. Each cubic centimeter of decinormal acid represents 30.09 mg of crystallized morphine. The morphine obtained by the above process represents 4 grams of opium. From these data can readily be calculated the per cent of morphine obtained, to which add 1.12 as a correction for the morphine remaining in the solvents used.

OPIUM ASSAYS, COMPARISON OF METHODS.

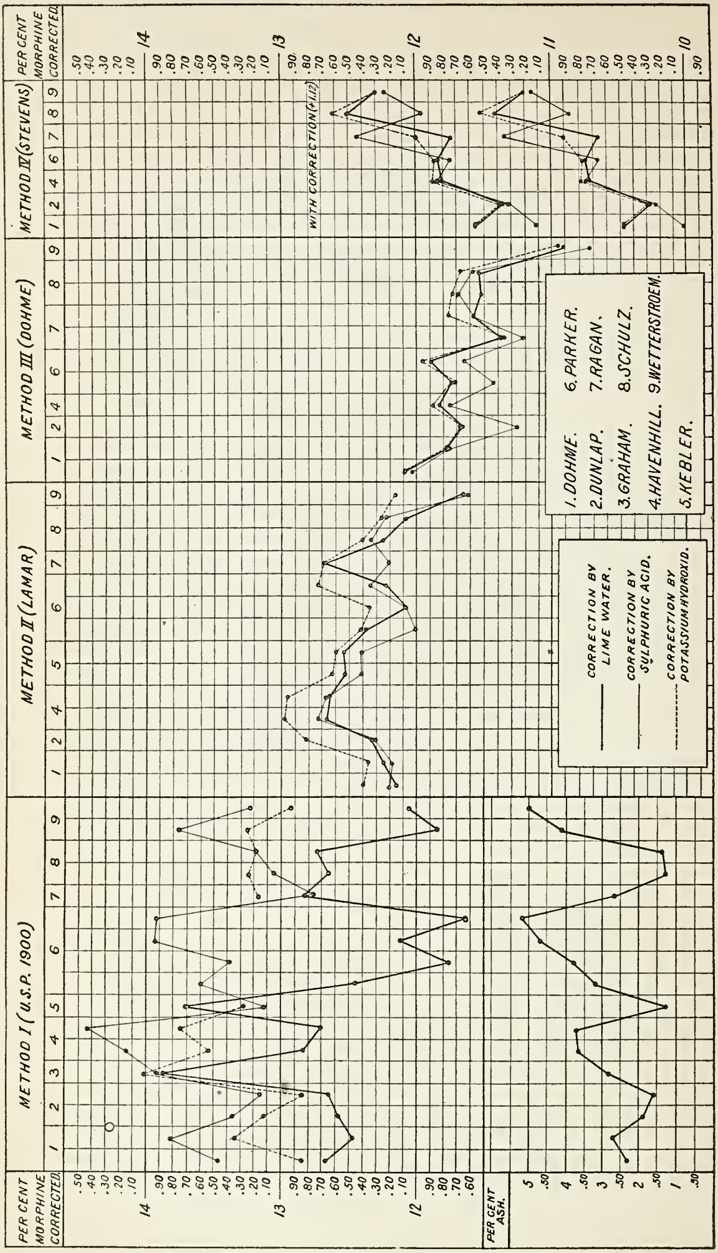

FIG. 2.—Graphic representation of variations in opium assays made by four different methods.

Table I.—*Opium assays by Method I, United States Pharmacopœia, 1900.*

Analyst.	Amount of morphine on filter paper.	Average.	Amount of morphine on watch glass.	Average.	Purity by limewater.	Purity by potassium hydroxid.	Purity by sulphuric acid titration.	Morphine in opium by lime water method.	Morphine in opium by potassium hydroxid method.	Morphine in opium by sulphuric acid titration.	Ash in morphine.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Dohme	13.98	13.86	13.86	13.77	91.98	93.20	97.80	12.67	12.84	13.47	2.33
Do	13.74		13.68								
Do	14.45	14.37	14.27	14.18	88.00	94.20	97.40	12.47	13.36	13.81	2.66
Do	14.28		14.09								
Dunlap	14.22	14.19	14.16	14.14	89.00	92.80	94.50	12.58	13.12	13.37	1.90
Do	14.15		14.12								
Do	13.90	13.80	13.85	13.74	92.00	93.50	95.80	12.65	12.85	13.16	1.60
Do	13.69		13.62								
Graham	14.47	......	14.43	14.43	96.20	97.10	96.50	13.88	14.01	13.92	2.80
Havenhill	14.70	14.65	14.59	14.52	88.49	93.20	97.46	12.85	13.54	14.15	3.67
Do	14.60		14.44								
Do	15.00	14.95	14.90	14.87	85.40	92.60	97.88	12.70	13.75	14.44	3.76
Do	14.90		14.83								
Kebler	13.96	14.01	13.81	13.86	98.90	95.80	94.60	13.71	13.28	13.11	1.30
Do	14.00		13.87								
Do	14.06		13.89								
Parker	14.25	[a]14.17	14.14	14.06	88.63	(c)	96.74	12.46	......	13.60	3.20
Do	14.10		14.05								
Do	14.30		14.16								
Do	14.03		13.90								
Do	14.06	[a]13.99	13.91	13.83	85.12	(c)	96.89	11.77	......	13.39	3.80
Do	13.92		13.74								
Do	14.61	......	14.44	......	......	......	......	......	......	......	......
Do	14.76	[a]14.69	14.59	14.59	83.03	(c)	95.56	12.12	......	13.94	4.70
Do	14.82		14.73								
Do	14.48		14.45								
Do	14.39	[b]14.44	14.21	14.28	81.40	(c)	97.49	11.62	......	13.92	5.20
Do	14.49		14.35								
Ragan	13.54	13.47	13.46	13.38	96.30	98.50	95.50	12.83	13.18	12.78	2.70
Do	13.40		13.30								
Schulz	13.23	13.34	13.21	13.32	95.00	99.40	98.10	12.65	13.23	13.06	1.30
Do	13.45		13.42								
Do	13.62	13.48	13.60	13.46	94.60	98.00	98.00	12.73	13.19	13.19	1.40
Do	13.33		13.32								
Wetterstroem	14.75	14.80	14.51	14.60	81.15	90.85	94.39	11.84	13.26	13.77	4.10
Do	14.84		14.70								
Do	14.85	14.81	14.30	14.25	84.84	90.68	92.86	12.06	12.93	13.23	5.00
Do	14.77		14.20								
Average	14.21	14.19	14.08	14.05	89.41	94.60	96.32	12.58	13.29	13.55	3.02
Maximum	15.00	14.95	14.90	14.87	98.90	99.40	98.10	13.88	14.01	14.44	5.20
Minimum	13.23	13.34	13.21	13.32	81.15	90.68	92.86	11.62	12.84	12.78	1.30
Difference	1.77	1.61	1.69	1.55	17.75	8.72	5.24	2.26	1.17	1.66	3.90

[a] Stood 24 hours.

[b] Stood 48 hours.

[c] Clear filtrate could not be obtained.

TABLE II.—*Opium assays by Method II, United States Pharmacopœia, Lamar's modification.*

Analyst.	Amount of morphine on filter paper.	Average.	Amount of morphine on watch glass.	Average.	Purity by limewater.	Purity by potassium hydroxid.	Purity by sulphuric acid titration.	Morphine in opium by lime water method.	Morphine in opium by potassium hydroxid method.	Morphine in opium by sulphuric acid titration.	Ash in morphine.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Dohme	12.48	12.53	12.34	12.40	98.00	100.00	98.45	12.15	12.40	12.20	......
Do	12.58		12.46								
Do	12.47	12.54	12.32	12.36	99.00	100.00	98.57	12.24	12.36	12.18	......
Do	12.60		12.39								
Dunlap	12.71	12.84	12.67	12.81	96.40	100.00	96.10	12.34	12.81	12.32	0.38
Do	12.97		12.95								
Havenhill	13.20	13.19	13.04	13.00	97.54	99.90	97.84	12.67	12.98	12.72	......
Do	13.18		12.95								
Do	13.17	13.15	13.02	12.97	97.40	99.90	97.84	12.64	12.96	12.67	.43
Do	13.12		12.92								
Kebler	12.80	12.72	12.68	12.62	99.20	100.00	98.30	12.52	12.62	12.40	.18
Do	12.63		12.56								
Do	12.63	12.69	12.55	12.60	99.40	100.00	98.50	12.53	12.60	12.41	.37
Do	12.74		12.65								
Parker	12.50	[a]12.54	12.37	12.43	99.68	99.90	96.74	12.38	12.41	12.02	.22
Do	12.57		12.48								
Do	12.53	[a]12.54	12.46	12.45	99.03	99.56	97.49				
Do	12.55		12.44								
Do	12.37	[a]12.51	12.25	12.40	97.40	99.70	97.41	12.08	12.36	12.08	.20
Do	12.65		12.54								
Do	12.97	[b]12.91	12.84	12.79	95.60	99.48	96.58	12.22	12.72	12.35	.24
Do	12.84		12.73								
Ragan	12.79	12.72	12.77	12.70	99.80	99.90	96.10	12.68	12.69	12.20	.46
Do	12.65		12.63								
Schulz	12.73	12.47	12.72	12.46	98.20	99.60	99.00	12.24	12.40	12.33	.90
Do	12.21		12.20								
Do	12.40	12.30	12.39	12.29	98.40	99.80	99.60	12.09	12.25	12.23	.50
Do	12.19		12.18								
Wetterstroem	12.96	12.77	12.35	12.17	95.65	100.00	95.50	11.64	12.17	11.60	.64
Do	12.77		12.01								
Do	12.68		12.15								
Average	12.70	12.69	12.55	12.56	98.05	99.85	97.60	12.33	12.56	12.29	.41
Maximum	13.20	13.19	13.04	13.00	99.80	100.00	99.60	12.68	12.98	12.72	.90
Minimum	12.19	12.30	12.01	12.17	95.60	99.48	95.50	11.64	12.17	11.60	.18
Difference	1.01	.89	1.03	.83	4.20	.52	4.10	1.04	.81	1.12	.72

[a] 24 hours standing.

[b] 48 hours standing.

TABLE III.—*Opium assays by Method III, United States Pharmacopœia, modified by Dohme.*

Analyst.	Amount of morphine on filter paper.	Average.	Amount of morphine on watch glass.	Average.	Purity by limewater.	Purity by potassium hydroxid.	Purity by sulphuric acid titration.	Morphine in opium by lime water method.	Morphine in opium by potassium hydroxid method.	Morphine in opium by sulphuric acid titration.	Ash in morphine.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Dohme	12.19	12.16	12.14	12.10	100.00	100.00	99.40	12.10	12.10	12.03	......
Do	12.12		12.06								
Do	11.92	11.94	11.76	11.78	100.00	100.00	99.88	11.78	11.78	11.76	......
Do	11.95		11.80								
Dunlap	11.63	11.68	11.62	11.66	100.00	100.00	96.60	11.66	11.66	11.27	......
Do	11.72		11.70								
Havenhill	11.93	11.92	11.89	11.89	99.46	99.99	98.84	11.83	11.89	11.76	0.23
Do	11.97		11.93								
Do	11.86		11.86								
Parker	11.77	[a]11.84	11.72	11.75	99.88	99.82	97.34	11.73	11.72	11.43	.18
Do	11.90		11.77								
Do	11.66	(a)	11.60	11.60	99.24	......	97.64	......	......	......	......
Do	11.99	[b]12.03	11.92	11.96	99.44	99.90	97.49	11.90	11.95	11.66	.06
Do	12.06		11.99								
Ragan	11.51	11.48	11.41	11.43	99.66	99.43	98.15	11.39	11.36	11.22	.24
Do	11.45		11.44								
Do	11.62	11.77	11.62	11.77	98.47	100.00	98.50	11.59	11.77	11.59	......
Do	11.92		11.91								
Schulz	11.72	11.78	11.72	11.78	97.80	99.60	99.30	11.52	11.73	11.69	.05
Do	11.83		11.83								
Do	11.80	11.72	11.79	11.71	98.60	99.80	99.00	11.54	11.68	11.59	......
Do	11.63		11.62								
Wetterstroem	11.01	11.12	10.74	10.95	99.60	99.80	98.00	10.90	10.94	10.73	......
Do	10.74		10.50								
Do	11.61		11.61								
Average	11.74	11.77	11.68	11.71	99.35	99.85	98.35	11.62	11.69	11.52	.15
Maximum	12.19	12.16	12.14	12.10	100.00	100.00	99.88	12.10	12.10	12.03	.24
Minimum	10.74	11.12	10.50	10.95	97.80	99.43	96.60	10.90	10.94	10.73	.05
Difference	1.45	1.04	1.64	1.15	2.20	.57	3.28	1.20	1.16	1.30	.19

[a] Stood 24 hours.

[b] Stood 48 hours.

Table IV.—*Opium assay by Method IV (Stevens's).*

Analyst.	Amount of morphine on filter paper.	Average.	Amount of morphine on watch glass.	Average.	Amount of morphine on cotton pledget.	Average.	Purity by lime water.	Purity by potassium hydroxid.	Purity by sulphuric acid titration.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Dohme	10.65	10.63	10.55	10.49			100.00	100.00	
Do	10.60		10.43						
Do					10.07	10.13			99.20
Do					10.19				
Dunlap	10.25	10.28					100.00	100.00	
Do	10.30								
Do					10.48	10.34			99.90
Do					10.20				
Havenhill	10.98	10.94	10.80	10.80			99.46	99.99	
Do	10.90		10.80						
Do					11.03	11.01			97.76
Do					10.98				
Parker	11.08	[a]10.89	11.00	10.84			99.30	99.50	
Do	10.70		10.68						
Do					10.93	11.04			96.60
Do					11.15				
Ragan	11.13	11.14					96.30	100.00	
Do	11.15								
Do	10.75	10.77	10.73	10.74			98.90	99.20	
Do	10.78		10.75						
Do					11.28	11.57			98.20
Do					11.85				
Schulz	11.63	11.57	11.62	11.55			98.80	99.80	
Do	11.50		11.47						
Do					10.54	10.89			99.75
Do					11.23				
Wetterstroem	12.46	11.31					99.20	99.00	
Do	10.15								
Do					11.50	11.15			100.00
Do					10.80				
Average	10.94	10.94	10.93	10.93	10.88	10.88	99.00	99.69	98.68
Maximum	12.46	11.57	11.62	11.55	11.85	11.57	100.00	100.00	99.90
Minimum	10.15	10.28	10.43	10.49	10.07	10.13	96.30	99.00	96.60
Difference	2.31	1.29	1.19	1.06	1.78	1.44	3.70	1.00	3.30

Analyst.	Without correction.			With correction factor 1.12.			Ash in morphine.
	Morphine in opium by lime-water method.	Morphine in opium by potassium hydroxid method.	Morphine in opium by sulphuric acid titration.	Morphine in opium by lime-water method.	Morphine in opium by potassium hydroxid method.	Morphine in opium by sulphuric acid titration.	
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Dohme	10.49	10.49		11.61	11.61		
Do			10.05			11.17	
Dunlap	10.28	10.28		11.40	11.40		
Do			10.24			11.36	
Havenhill	10.74	10.79		11.86	11.86		0.28
Do			10.75			11.87	
Parker	10.76	10.78		11.88	11.90		
Do			10.66			11.78	
Ragan	10.72	11.14		11.84	12.26		
Do	10.62	10.66		11.74	11.78		
Do			11.36			12.48	
Schulz	11.41	11.53		12.53	12.65		.10
Do			10.87			11.99	
Wetterstroem	11.20	11.20		12.32	12.32		
Do			11.15			12.27	
Average	10.70	10.75	10.85	11.82	11.87	11.97	
Maximum	11.41	11.58	11.36	12.53	12.65	12.48	
Minimum	10.28	10.28	10.05	11.40	11.40	11.17	
Difference	1.13	1.25	1.31	1.13	1.25	1.31	

[a] Stood twenty-four hours.

The results, as recorded in the tables and as graphically represented, are full of interest for the alkaloidal chemist. The average difference between weighing the morphine on filter papers direct and on watch glasses after removal is, for Methods I and II, 0.06 per cent; for Method III, 0.15 per cent, and for Method IV, 0.23 per cent. These results certainly show, as in last year's work on opium, that there is nothing gained by removing the morphine from the filter paper to the watch glass before weighing in Methods I and II The time and trouble involved by such a procedure may therefore be saved.

The variations in the amounts of impurities contained in the morphine obtained by the several workers amounted in Method I, by limewater, to 17.75 per cent; by potassium hydroxid, 8.72 per cent; by titration, 5.24 per cent. For Method II, with limewater, 4.20 per cent; for potassium hydroxid, 0.52 per cent, and by acid titration, 4.10 per cent. For Method III, with limewater, 2.20 per cent; for potassium hydroxid, 0.57 per cent, and by acid titration, 3.28 per cent. For Method IV, with limewater, 3.70 per cent; with potassium hydroxid, 1 per cent, and by acid titration, 3.30 per cent.

These results clearly show that the morphiometric assay method of the 1890 Pharmacopœia is unreliable. The limewater correction, as directed by the eighth revision of the United States Pharmacopœia certainly enables the several workers to obtain more uniform results, as is shown by the average differences obtained, namely, 2.26 per cent for limewater; 1.17 per cent for potassium hydroxid, and 1.66 per cent for acid titration. While the average differences obtained by these various correction factors are markedly in excess of those usually allowed in commercial transactions, there is certainly a decided improvement over the method as originally outlined in the 1890 Pharmacopœia. It has long been known that morphine crystallized from the various grades of opium, in the regular course of assay, carries with it more or less foreign matter, but why such varying amounts of impurity should be obtained from the same opium in the hands of different analysts, supposedly under the same conditions, is difficult of explanation. Some of the factors which undoubtedly influence the amount of impurity are, (1) the difference in time allowed by the various workers for the precipitation of the morphine; (2) the temperature at which the morphine is crystallized out, and (3) the different degrees of agitation employed by the various operators.

It has been observed in the drug laboratory of the Bureau of Chemistry that different degrees of agitation employed in shaking out the morphine have a decided influence on the purity of the resulting morphine. Vigorous agitation produces purer morphine than simply shaking the flask well. The longer the time allowed for crystallizing out the morphine, the greater the amount of impurity associated with the morphine. The great variation in the amount of ash obtained by the various workers is remarkable. The high per cent obtained by Parker is undoubtedly due to excessive length of time allowed for precipitation.

There is a marked relation between the amount of morphine indicated by acid titration and the amount of ash present, which clearly shows that the impurity represented by the ash possesses some basic properties. The results obtained by acid titration of morphine during the past two years of cooperative work, coupled with past experience, clearly show that pure morphine can be satisfactorily titrated with acid solutions, but such titrations are unreliable with impure morphine, such as is commonly obtained by the 1890 pharmacopœial method. The potassium hydroxid method has also been found wanting. These two methods of correction will therefore not be accorded additional trial under the present conditions of opium assaying.

The average per cent of morphine obtained by the four methods employed, using limewater as correcting agent, are as follows: Method I, 12.58; Method II, 12.33; Method III, 11.62, and Method IV, with correction factor 1.12, 11.82; without this correction factor, 10.70. These results clearly show that Methods I and II are the most satisfactory, so far as per cent of pure morphine is concerned. Method III requires practically as much time for execution as Methods I and II, with a lower yield of morphine; this method must be considered inferior to either of the other two methods. Method IV can be executed in much less time than either one of the other three methods, which is an important desideratum, but the results, even with the correction factor 1.12, are considerably below those of Methods I and II. It possesses an additional advantage over Method I in that it gives more uniform results, but in this respect it is not equal to Method II, which gives the most uniform results of all the methods considered thus far. Method II gives not only the most uniform results, but after excluding the lowest result for limewater and acid titration the greatest differences are 0.6 and 0.7 per cent, respectively—differences which very closely approach the permissible variation between workers. In addition to giving closely agreeing results, Method II yields on the average only 0.25 per cent less of morphine than Method I, both based on limewater correction.

It is recommended:

(1) That the method recognized by the present Pharmacopœia, eighth revision, for the assaying of opium be adopted as a provisional method by the Association of Official Agricultural Chemists.

(2) That the cooperative work on the assaying of plant products be extended to other drugs.

REPORT OF COMMITTEE C ON RECOMMENDATIONS OF REFEREES.

By A. L. Winton, *Chairman.*

(Food adulteration.)

(1) Saccharine Products.

It is recommended—

1. That the methods of Circular 23, Bureau of Chemistry (Methods for the examination of maple products, Hortvet), be adopted as provisional.

Adopted.

(2) Vinegar.

It is recommended—

1. That the following words in Bulletin 65, page 68, be eliminated: "The presence of malic acid distinguishes cider vinegars, though the quantity is often small." * * * "If a precipitate be obtained, parallel tests with silver nitrate and barium chlorid to determine the absence of chlorids and sulphates should be made before the presence of malic acid be considered proved." (Referred to committee, on motion by Mr. Tolman.)

Adopted.

(3) Flavoring Extracts.

It is recommended—

1. That Leach's test for coumarin be adopted as a provisional method. (See Leach, Food Inspection and Analysis, p. 738.)

Adopted.

2. That the colorimetric ferrous sulphate method for determination of vanillin be adopted as a provisional method. (Ibid., p. 735.)

Adopted.

3. That Winton and Bailey's modification of the Hess and Prescott method for the determination of vanillin, coumarin, and acetamid be substituted for the present gravimetric methods. (J. Amer. Chem. Soc., 1899, *21:* 256; 1902, *24:* 1128; 1905, *27:* 719.)

Adopted.

4. That Leach and Lythgoe's refractometric method for the detection of methyl alcohol be adopted as a provisional method in the analysis of extracts. (J. Amer. Chem. Soc., 1905, *27:* 964.)

Adopted.

5. That the recommendations of the associate referee on flavoring extracts in regard to work for the following year be adopted:

(*a*) A thorough test of the present methods for the determination of citral in oil of lemon.

(*b*) Application to extracts of the methods for the detection of caramel as applied to whiskies.

(*c*) Application of a method for measuring the purity of extracts by means of the volume of their lead acetate precipitate.

(*d*) Effect of the presence of glycerin on the precipitation of the resins.

(*e*) Study of the crystalline forms of vanillin and coumarin.

Adopted.

(4) DAIRY PRODUCTS.

It is recommended—

That the Zeiss immersion refractometer method (Leach and Lythgoe) be adopted as a provisional method for the determination of added water in milk. (See p. 83.)

Adopted.

(5) SPICES.

It is recommended—

That the methods for the analysis of prepared mustard, as outlined in the report of the associate referee (p. 73), be adopted as provisional methods.

Adopted.

(6) FATS AND OILS.

It is recommended—

1. That the Hanus method, as given in the Proceedings for 1903[a], be adopted as official for the determination of the iodin absorption of oils and fats.

2. That the method for the titer test be adopted as provisional. (See Circular 27, Bureau of Chemistry, U. S. Dept. Agr.)

Adopted.

3. That the following recommendations for work for next year be adopted:

(*a*) Study of methods for determination of moisture and impurities in fats.

(*b*) Study of method for making total fatty acid determination in soap stock.

(*c*) Study of method for cold test.

(*d*) Further study of drying of fatty acids in the titer test.

(*e*) Further study of the Belfield test.

Adopted.

4. That the recommendation made at the association meeting in 1903 (Bul. 81, p. 64) for changing the correction for temperature for index of refraction from 0.000176 to 0.000365 now be made official. (Bul. 46, revised, p. 49.)

Adopted.

(7) PRESERVATIVES.

It is recommended—

1. That Arnold and Mentzel's method for the detection of formaldehyde (using phenylhydrazin hydrochlorid and ferric chlorid) be adopted provisionally. (Bul. 90, p. 47, Method 5; Zts. Nahr. Genussm., 1902, *5:* 353.)

2. That Arnold and Mentzel's method for the detection of formaldehyde (using phenylhydrazin hydrochlorid and potassium ferricyanid) be adopted provisionally. (Bul. 90, p. 48, Method 6; Chem. Ztg., 1902, *26:* 246; abs. J. Chem. Soc. (Lond.), 1902, (2), *82:* 367; abs. Chem. Centrbl., 1902, pt. 1, p. 1077.)

3. That the Rimini test for the detection of formaldehyde be adopted provisionally. (Bul. 90, p. 48, Method 7; Ann. di Farmacal., 1898, p. 97; abs. Chem. Centrbl., 1898, pt. 1, p. 1152; abs. J. Soc. Chem. Ind., 1898, *17:* 697.)

4. That the colorimetric method for the determination of salicylic acid be adopted as a provisional method. (Compt. rend., 1881, p. 278.)

5. That the methods suggested by the referee for the quantitative determination of salicylic acid, benzoic acid, and saccharin by weighing and titrating the residue from

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 81, p. 63.

extraction and sublimation (after previous separation by distillation when necessary) be adopted provisionally. (Bul. 90, p. 59, Methods 2, 3 and 4.)

6. That the Blarez method for the detection of fluorids, as modified by Leach, be adopted as a provisional method. (Chem. News, 1905, *91:* 39; Ann. Rept. Mass. State Bd. of Health, 1905.)

7. That the method for the detection of fluorids, borfluorids, and silicofluorids directly from the ash be provisionally adopted. (Bul. 59, p. 63.)

8. That the rearrangement of the provisional methods for the detection of preservatives suggested by the referee be adopted.

Recommendations 1–8 were adopted.

(8) Distilled Liquors.

It is recommended—

1. That the Trillat test for the detection of methyl alcohol in distilled liquors be added to the provisional methods. (See p. 57.)

2. That the Riche and Bardy test for the detection of methyl alcohol in distilled liquors be added to the provisional methods. (See p. 57.)

3. That the method of Leach and Lythgoe for the estimation of ethyl and methyl alcohol in mixtures of the same be adopted as a provisional method. (See p. 58.)

4. That the method given in the referee's report (p. 58), as recommended by Mr. Tolman, for the determination of ethereal salts, be substituted for the method given in Bulletin 65, page 98.

Adopted.

5. That the method given on page 58 of the referee's report, as recommended by Mr. Tolman, for the determination of aldehydes, be substituted for the method given in Bulletin 65, page 97.

Adopted.

6. That the method given on page 58 of the referee's report, as recommended by Mr. Tolman, for the determination of furfurol, be substituted for the method given in Bulletin 65, page 98.

Adopted.

7. That the method for fusel oil recommended by Mr. Tolman and quoted by the referee (p. 58) be given a trial by the association.

Adopted.

8. That the test for determining artificial coloring matter in whisky, as recommended by Mr. Tolman and quoted by the referee (p. 59), be tried.

Adopted.

9. That for the next year's work the referee make a further study of tests for artificial coloring matter and for the determination of fusel oil.

Adopted.

(9) Water.

To provide for the systematic test of the method of Benedict and Manning and of Maquenne's method for determining hygroscopic moisture, in accordance with the resolution passed instructing the referee on food adulteration to have such work done, the appointment of an associate referee for the determination of water in foods was recommended and adopted.

REPORT ON THE SEPARATION OF MEAT PROTEIDS.

By W. D. Bigelow, *Associate Referee.*

The chief problems still unsolved relative to the examination and valuation of meat extracts are:

(1) To separate the proteoses and peptones from the simpler amido bodies (the so-called meat bases).

(2) To distinguish gelatin and the products of its hydrolysis from proteoses, peptones, and the meat bases.

(3) To distinguish between true peptones and "false peptones" formed by the action of steam on proteid compounds.

(4) To distinguish yeast extracts from meat extracts and detect mixtures of the same.

It is, of course, of the first importance to distinguish products of the general class of fluid beef and beef juice from the extracts, but it is believed that the solution of the questions mentioned above will yield the data necessary to make such distinctions. The work during the last year has been confined to a study of the tannin salt method for the precipitation of proteoses and peptones, that method having in previous years given the best results for this separation.

PRELIMINARY WORK.

It was found impossible to secure any collaboration from other laboratories, and the work here reported was done by the associate referee and Mr. F. C. Cook. Some preliminary work was done in order to compare again the results given by phosphotungstic acid and zinc sulphate. In this work the phosphotungstic acid precipitate was obtained in the cold by Stutzer's method. The results of this preliminary experiment are given in Table I. It is evident in all cases that none of the nitrogen of the various amido bodies used is precipitated by zinc sulphate. This conclusion is now commonly accepted and is only offered here as confirmatory of previous work on the subject. In the case of phosphotungstic acid it has been believed that while the diamido bodies were precipitated partly or completely the monoamido bodies were not precipitated. In Table I it is apparent that a considerable portion of the diamido bodies is precipitated, and in some cases precipitation appears to be practically complete.

TABLE I.—*Nitrogen precipitated by phosphotungstic acid and zinc sulphate from mixtures of Witte's peptone or somatose and amido bodies.*

Nitrogen contained and determined.	Witte's peptone.	Witte's peptone, leucin, and tyrosin.	Leucin and tyrosin precipitated.	Witte's peptone.	Witte's peptone, glycocoll creatin, and creatinin.	Glycocoll, creatin, and creatinin precipitated.
	Gram.	*Gram.*	*Gram.*	*Gram.*	*Gram.*	*Gram.*
Nitrogen content of Witte's peptone or somatose	0.0714	0.0714	....	0.0762	0.0762	....
Nitrogen content of solution of amido bodies	....	[a].0045	....	....	.0171	....
Nitrogen precipitated by phosphotungstic acid	.0655	.0683	0.0028	.0695	.0790	0.0095
Nitrogen precipitated by zinc sulphate	.0404	.0407	.0003	.0498	.0475	....

Nitrogen contained and determined.	Somatose.	Somatose, glycocoll, leucin, tyrosin, xanthin, hypoxanthin, and guanin.	Glycocoll, leucin, tyrosin, xanthin, hypoxanthin, and guanin precipitated.	Somatose.	Somatose, glycocoll and glutamin.	Glycocoll and glutamin precipitated.
	Gram.	*Gram.*	*Gram.*	*Gram.*	*Gram.*	*Gram.*
Nitrogen content of Witte's peptone or somatose	0.0619	0.0619	....	0.0619	0.0619	....
Nitrogen content of solution of amido bodies	....	.0106	....	....	.0129	....
Nitrogen precipitated by phosphotungstic acid	.0594	.0637	0.0043	.0585	.0604	0.0019
Nitrogen precipitated by zinc sulphate	.0545	.0547	.0002	....	....	....

[a] Leucin 0.0025 gram and tyrosin, 0.0020 gram.

It is also apparent, however, in Table I, at least in the case of glycocoll and glutamin, that these monoamido bodies are partly precipitated by phosphotungstic acid in the cold. It is evident therefore that this reagent may not answer for the separation of proteid bodies in the presence of any considerable amounts of either the diamido or monoamido bodies.

COMPARISON OF THE ACTION OF PHOSPHOTUNGSTIC ACID HOT AND COLD AND TANNIN SALT ON MEAT BASES.

In 1903 the referee reported the results of work done with Mr. Harcourt[a] on precipitations obtained by various reagents with a number of amido bodies found in the extractives from meats and vegetables, as well as some synthetic products of the same class. At that time, however, no examination was made of the tannin-salt method. During the past year this work has been repeated and results obtained by the application of the tannin-salt method to a number of the more important amido bodies. These results are given in Table II. In this work two tannin-salt solutions were used differing from each other in the content of both tannin and sodium chlorid.

Table II.—*Action of proteid precipitants on amido bodies.*

Amido body.	Tannin salt.[a]	Tannin salt.[b]	Phosphotungstic acid, cold.	Phosphotungstic acid, hot (96° C.).
Glycocoll	Cloud	None	None	None.
Alanin	do		do	Do.
Creatin	Slight ppt	Rather heavy ppt	White granular ppt	Do.
Glutaminic acid	Cloud	None	None	Do.
Aspartic acid	None	do	do	Do.
Allantoin	do	do	do	Do.
Asparagin	do	do	do	Do.
Betain	do		Flaky white ppt	Do.
Creatinin	Slight turbidity	None	White granular ppt	Do.
Glutamin	Cloud	do	None	Do.
Guanin	None	do	do	Do.
Xanthin	do		do	Do.
Hypoxanthin	do		White granular ppt	Do.
Leucin	do	None	None	Do.
Trimethylamin	Heavy ppt	do	White ppt[c]	Do.
Diphenylamin	None		None	Do.
Phenylenediamin	Black flaky ppt	Brown flaky ppt	A heavy white ppt	Brownish ppt.
Acetamin	None	None	None	None.
Sarcosin		do		

[a] 4 grams of sodium chlorid and 10 cc of 12 per cent tannin per 100 cc.
[b] 15 grams of sodium chlorid and 20 cc of 12 per cent tannin per 100 cc.
[c] This disappeared on standing 2 or 3 minutes.

After the completion of some work to be described later, which indicated that stronger solutions of both tannin and salt should be employed, this work was repeated, using 30 cc of 24 per cent tannin and 15 grams of salt in 100 cc of a solution of the amido bodies. By consulting Table II it will be seen that with a more dilute tannin salt solution precipitates were obtained with creatin, trimethylamin, and phenylenediamin. These results were confirmed with the stronger solution of tannin salt, which gave no precipitate except in the cases mentioned. The weaker solution also gave a slight turbidity, but insufficient to indicate the precipitation of a determinable amount of nitrogen with glycocol, alanin, glutamic acid, creatin, and glutamin. It is probable that failure to obtain this turbidity with the stronger tannin salt solution is due to the increased difficulty of detecting a turbidity in that solution, and not to the solvent action of the stronger solution on the slight amount of material precipitated in the more dilute solution. Considering the fact that this turbidity was not detected in the stronger solution, and therefore at least was not increased by increasing the strength of the reagent, it is suggested that this was due not to the insolubility of the amido bodies in question in the presence of the tannin salt solution, but rather to a small amount of impurity contained in the preparations examined. It is apparent, however, that creatin, trimethylamin, and phenylenediamin can not be separated by this method from peptones. In the case of creatin this is a serious matter, since that substance is the meat base which occurs most abundantly in meat and meat extract.

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[a] U. S. Dept. Agr.. Bureau of Chemistry, Bul. 81, p. 106.

It appears, however, that the error due to creatin can be eliminated by determining the amount of creatin present before and after the precipitation with the tannin-salt reagent. The method for this determination will be discussed later. It is believed that phenylenediamin does not occur in meat extract, and that in the examination of meat products, the fact that this substance is precipitated by the tannin-salt reagent may be disregarded. It is probable that trimethylamin does not occur in meat, but it does occur in a considerable quantity in fish and in the beet root. This method of separation therefore is not of such universal application in the presence of this amido body as could be desired.

It was stated above that the error occasioned by the precipitation of a proportion of the creatin of the tannin-salt reagent may be corrected by determining the creatin before the application of the tannin-salt reagent, and in the filtrate from the precipitate given by that reagent. At the suggestion of Prof. L. B. Mendel, Mr. Cook studied the applicability of Jaffe's [a] reaction to this determination. It appears that the percentage of creatin can be readily determined by Folin's method [b] for the estimation of creatin in urine, based on the reaction given above.

It was found impossible to purify the extracts by means of either basic lead acetate or charcoal, the traces of the former remaining after treatment with potassium sulphate, interfering with the color, and the charcoal removing a considerable portion of the creatinin from the solution. The determinations of creatin and creatinin were made in samples of commercial meat extract by Folin's method, as well as the same determinations in the sample of the same extract to which known amounts of creatin had been added. The increased reading, owing to the addition of creatin, was sufficiently close to the theoretical to be entirely satisfactory. It has been found necessary, however, to assume that the original reading of the meat extract was correct. This work is being continued and a thorough examination of creatin in meat and meat extract is under investigation.

TABLE III.—*Action of proteid precipitants or mixtures of amido bodies.*

Amido bodies.	Tannin and salt.[a]	Phosphotungstic acid.	
		Cold.	Hot (96° C.).
Leucin Glycocoll	Very slight cloud	None	None.
Aspartic and glutaminic acid.	Slight cloud	do	Do.
Acetamid Betain	None	do	Do.
Creatin Creatinin	Slight cloud	Heavy white ppt	Do.
Allantoin Asparagin	None	None	Do.
Xanthin Hypoxanthin	Faint cloud	Heavy white ppt	Slight ppt.
Guanin Glutamin	None	None	None.
Trimethylamin Diphenylamin	Heavy yellow brown ppt.	Granular white ppt	Granular white ppt.

[a] Four grams of sodium chlorid and 10 cc of 12 per cent tannin per 100 cc.

Of the amido bodies used the hot phosphotungstic acid solution only precipitated phenylenediamin. Phosphotungstic acid in the cold was found to give heavy precipitations with creatin, beatin, hypoxanthin, trimethylamin, and phenylenediamin. The effect of the reagents mentioned on mixtures of the amido bodies included in Table I was then studied. The results are given in Table III. This work was completed before we discovered the insufficiency of the tannin-salt solution first used and the strong tannin-salt solution was not employed. It will be seen that in no case was a precipitate given by the action of any reagent on a mixture of two amido bodies, neither of which was precipitated separately by that reagent.

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[a] Zts. physiol. Chem., 1886, *10:* 391.

[b] Ibid., 1904, *41:* 223.

ACTION OF TANNIN-SALT ON MEAT BASES IN THE PRESENCE OF PROTEOSES AND PEPTONES.

In order to examine further the reliability of the tannin-salt method for the determination of proteoses and peptones in the presence of the simple amido bodies mixtures were prepared of somatose and several of the more common meat bases. The results of this work are given in Table IV.

TABLE IV.—*Nitrogen precipitated from mixtures of somatose and meat bases by tannin [a] salts.*

Substance.	Nitrogen in somatose used.	Nitrogen in amido bodies used.	Total nitrogen precipitated.	Amido nitrogen precipitated.
	Grams.	*Grams.*	*Grams.*	*Grams.*
Blank	0.1006	None.	0.0966	None.
Phenylenediamin	.1006	0.0230	.1040	0.0074
Creatin	.1006	.0494	.1080	.0114
Creatinin	.1006	.0090	.0984	.0018
Glycocoll	.1006	.0202	.0966	None.
Sarcosin	.1006	.0270	.0956	−.0010
Allantoin	.1006	.0348	.0994	.0028
Leucin	.1006	.0034	.0966	None.

[a] Reagent employed contained 10 grams of sodium chlorid and 24 grams of tannin per 100 cc of the solution in which the precipitation occurred. The temperature was at 12° C.

Quantities of 0.8 gram each of somatose were mixed with several of the more important meat bases, and the nitrogen determined in the material precipitated by the tannin-salt reagent from the mixture. The reagent employed for this purpose was the strongest solution mentioned above; that is, it contained 10 grams of sodium chlorid and 2.4 grams of tannin per 100 cc of the solution in which the precipitation occurs. The temperature was at 12° C.

It will be seen that in only two cases was an appreciable quantity of nitrogen obtained in the precipitate in excess of that obtained with the somatose alone. In the presence of phenylenediamin this was equal to 0.0074 gram of nitrogen, or about one-third of the amount present in the amido body. In the presence of creatin containing 0.0494 gram of nitrogen, a little less than one-fourth of that amount, or 0.0114 gram of nitrogen, was precipitated by the reagent. In the case of the other amido bodies studied the nitrogen in the precipitate from the tannin-salt reagent was so nearly equal to that of the blank that it may be ignored as due to inaccuracies of the method.

EFFECT OF TEMPERATURE ON PRECIPITATION.

In previous years we have commented on the solubility of the tannin-salt precipitate and upon the necessity on that account of observing carefully an arbitrary method for that determination. It would appear, however, that a much higher degree of accuracy could be obtained by determining the solubility of the precipitate under known conditions and applying a correction therefor. From some experimental work done for that purpose it appeared that the amount of the precipitate obtained varied with the amount of tannin, the amount of salt, the temperature, and the volume of solution. It is found impracticable in the presence of a considerable amount of precipitable matter to determine with accuracy the quantity of reagent necessary to make precipitation complete. It was found also that by increasing the salt solution, even to a concentration far below that at which the precipitation of the ordinary proteids with sodium chlorid occurs, the amount of nitrogen precipitated by the tannin-salt solution was largely increased. It was also found that any great change in volume made a considerable change in the quantity of nitrogen precipitated. It is thought probable, therefore, that the solubility of the precipitate would depend to some extent on the temperature at which the precipitation was effected, and to determine this question precipitations with varying amounts of salt and tannin were made at three temperatures:

(1) In a refrigerator at about 12°.
(2) At room temperature, the precipitate standing over night at about 23°.
(3) In a drying oven heated with a thermostat, the temperature regulated at about 40°.

It was found that higher results were obtained with a lower temperature and that the nitrogen precipitated at room temperature was greater than that precipitated at 40° C. Moreover, the lower the temperature, the clearer was the supernatant liquid and the more complete the precipitation. The supernatant liquid in the case of the precipitations made at 40° C. was quite commonly turbid, and in many cases filtration was entirely impracticable. In the case of the precipitations made at room temperature the supernatant liquid though usually clear was occasionally turbid and filtration difficult. With the precipitations made in the refrigerator at a temperature of about 12° the supernatant liquid was almost always clear and the filtrations (which were also conducted in the refrigerator) rapid and satisfactory, leaving a perfectly clear filtrate.

COMPARISON OF VARIOUS TANNINS.

Different samples of tannin do not give uniform results with a given mixture of proteids and meat bases. The difference in some cases is so great as to lead to considerable inaccuracy, and it is of course essential that a uniform tannin be used in the prosecution of any particular investigation. At the same time there has been nothing in our experience to indicate that this difference is so great as to preclude the practicability of comparing in a general way the work of different laboratories. The lack of uniformity is considerable, however, and impairs the value of such a comparison. The results of this study are given in Tables V and VI. One important consideration that appears to have been overlooked is the nitrogen content of tannin. As will be seen in Table VI the amount of nitrogen contained in some samples of tannin is considerable, and a correction must always be made. The varying amount of the nitrogen in the tannin is either insoluble in water, or is precipitated from a tannin solution by sodium chlorid, and hence is insoluble in the tannin-salt reagent. It is important that blanks be run with the reagents employed, and that a correction be employed for the total nitrogen in the tannin employed as well as the nitrogen insoluble in the tannin-salt reagent.

TABLE V.—*Comparison of the precipitating power of two tannins on 1 gram of somatose in the presence of varying amounts of salt.*

Tannin solution.	Sodium chlorid.	Nitrogen precipitated.	Difference in nitrogen precipitated.
	Per cent.	*Gram.*	*Gram.*
A[a]	7	0.1127	0.0026
B[b]	7	.1153	
A	10	.1132	.0021
B	10	.1153	
A	15	.1143	.0026
B	15	.1169	
A	20	.1159	.0022
B	20	.1181	

[a] Solution A is a 12 per cent solution of an old sample of tannin; nitrogen per 10 cc=0.0020 gram.

[b] Solution B is a 24 per cent tannin solution diluted to 12 per cent; nitrogen per 10 cc=0.0012 gram.

In Table VI are given the results of the influence of reagents prepared from three samples of tannin upon solutions of somatose. In all cases the volume of the liquid in which the precipitation occurred was 100 cc, and contained 2.49 grams of tannin and 10 grams of salt. In the three samples the amount of nitrogen varied from 0.1155 to 0.1191 gram. The nitrogen content of the tannin itself must also be taken into consideration. This is a factor which we have only recently considered in connection with this work, but the amount of nitrogen has been found so great that it should always be determined and a correction applied. The three samples mentioned were found to contain from 0.0007 to 0.0052 gram of nitrogen in 20 cc of the sample.

TABLE VI.—*Nitrogen in tannin reagent.*[a]

Reagent.	Total nitrogen.	Nitrogen precipitated.	Nitrogen in 2.49 grams of tannin used.
	Gram.	*Gram.*	*Gram.*
Tannin, Merck's	0.1249	0.1191	0.00068
Tannin, Power's and Weightman's	.1249	.1165	.00112
Tannin, old sample, no label	.1249	.1155	.0052
Tannin, Mallinckrodt's	.1249	....	.0104

[a] All tannin solutions were made 12 per cent and 20 cc used in each case. Ten grams of salt were also added and one gram of somatose used. Ice box temperature, 12°.

To further study this question the nitrogen precipitate was obtained on quantities of 1 gram of somatose, using the tannin-salt precipitate prepared from two of the above lots of tannin. The results are given in Table V. In all cases the precipitations occurred in 100 cc of liquid, which contained 12 grams of tannin and the amount of sodium chlorid given in the table. It will be seen that the error due to the different precipitating powers of the two tannins is of considerable magnitude. In all cases in both Tables V and VI the quantity of nitrogen contained in the tannin itself has been allowed for, and is not responsible for the difference shown in the precipitating power of the various tannins.

PRESERVATION OF TANNIN-SALT REAGENTS.

It is well known that tannin undergoes fermentation and loses to a large extent its power of precipitating proteids. We have found that this occurs even in the presence of a considerable quantity of salt, and that the tannin-salt reagent should be kept in a cool place, and should not stand more than a few days before using.

NITROGEN PRECIPITATED BY VARYING QUANTITIES OF SALT AND TANNIN.

The varying results obtained with different strengths of salt and tannin suggested the advisability of determining whether there was any degree of concentration for both salt and tannin at which slight changes in concentration would be without material influence upon the results. To determine this the amount of nitrogen precipitated by tannin salt was determined in solutions whose sodium chlorid content varied from 0.8 to 26 grams per 100 cc, and whose tannin content varied from 0.63 to 10 grams per 100 cc.

When this work was undertaken it was believed that a concentration above 15 grams of sodium chlorid per 100 cc would not increase the nitrogen precipitated by the tannin-salt reagent until the sodium chlorid became so concentrated as to become a precipitate itself for some of the proteid bodies present For that reason the precipitations were made at more frequent intervals below 15 grams per 100 cc, and especially below 7 grams per 100 cc, where it was believed that the results would be practically constant.

An inquiry of this sort is greatly complicated owing to the fact that pure solutions of the proteid bodies can not be obtained. We have found it necessary to study those conditions which would give the maximum results with as pure solutions as were obtainable of proteoses and peptones, and then to use under such conditions solutions of the various meat bases in order to determine whether the latter were precipitated thereby.

An inspection of Tables VII and VIII will show that approximately the maximum results were obtained by using about 15 grams per 100 cc of sodium chlorid and 4 or 5 grams per 100 cc of tannin; that is, the proteid bodies under examination are dissolved in a small amount of water and concentrated solutions of sodium chlorid and tannin added in sufficient amount to form solutions of the concentration given above. It also appears from Tables VII and VIII that a considerable excess of tannin may be employed without any tendency of the reagent to dissolve the precipitates formed in excess.

Table VII.—*Amount of nitrogen precipitated from Armour's Extract (total nitrogen in 20 cc=0.1780 gram) by varying amounts of tannin and salt.*

[Ice box temperature, 12° C.; total volume, 100 cc.]

Sodium chlorid per 100 cc.	Grams of tannin in varying amounts of 12 per cent solution used.																
	10 cc= 1.25 grams.	11 cc= 1.37 grams.	12 cc= 1.50 grams.	13 cc= 1.62 grams.	14 cc= 1.75 grams.	15 cc= 1.87 grams.	16 cc= 2.00 grams.	18 cc= 2.25 grams.	20 cc= 2.50 grams.[a]	25 cc= 3.12 grams.	30 cc= 3.75 grams.	35 cc= 4.37 grams.	40 cc= 5.00 grams.	50 cc= 6.25 grams.	60 cc= 7.50 grams.	70 cc= 8.75 grams.	80 cc= 10.00 grams.
Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
1	0.0831	0.0838	0.0838	0.0849		0.0856	0.0862	0.0880	0.0899		0.0921						0.0959
2																	
3	.0819	.0838	.0832	.0849	0.0850	.0878	.0878	.0912	.0900		.0927						
4																	
5	.0809	.0838	.0866	.0871	.0855	.0868	.0885	.0880	.0887		.0909			0.0951			.1015
6																	
7	.0825	.0826	.0848	.0877	.0867	.0878	.0863	.0879	.0921		.0964						
8	.0826	.0838	.0860	.0849		.0868	.0878	.0879	.0909		.0909						
9	.0831	.0841	.0842	.0860	.0871	.0872	.0890	.0880			.0965						
10	.0825	.0859	.0876	.0855	.0872	.0873	.0863	.0898			.1191			.0997			
11	.0847	.0854	.0860	.0955	.0884	.0906	.0896	.0907	.0921		.0983						
12																	
13	.0847	.0869	.0876	.0871	.0884	.0884	.0897	.0902									
14																	
15	.0847	.0866	.0878	.0882	.0883	.0896	.0913	.0936	.0923 .0937	0.0937	.0950 .0999		0.1036		0.1009	0.1043	.1083
16																	
17									.0939	.0982	.0985	0.0982	.1070	.1051	.1087		
18																	
19																	
20						.0928			.0967 .0971		.1013		.1060	.1109			
21																	
22									.0985	.1010							
23																	
24																	
25						.0980			.1021		.1079						

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[a] From this point on in the majority of cases a 24 per cent solution was used diluted one-half, the resulting strength being the same as that indicated in the table.

Table VIII.—*Amount of nitrogen precipitated from one gram of somatose (total nitrogen=0.1249 gram) by varying amounts of tannin and salt.*

[Temperature, 12° C.; total volume, 100 cc.]

Sodium chlorid per 100 cc.	Grams of tannin in varying amounts of 12 per cent solution used.														
	5 cc= 0.63 gram.	10 cc= 1.25 grams.	11 cc= 1.37 grams	12 cc= 1.50 grams.	13 cc= 1.62 grams.	14 cc= 1.75 grams.	15 cc= 1.87 grams.	20 cc= 2.50 grams.[a]	25 cc= 3.12 grams.	30 cc= 3.75 grams.	35 cc= 4.37 grams.	40 cc= 5.00 grams.	50 cc= 6.25 grams.	60 cc= 7.50 grams.	70 cc= 8.75 grams.	80 cc= 10.00 grams.
Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
0.8	**0.0744**	**0.1014**					**0.1081** .1111	**0.1086** .1126		**0.1092** .1152						
1.0													0.1167	0.1173		0.1157
2.0														.1161	0.1167	
3.0																
4.0							**.1036** .1063	**.1097** .1137		**.1097** .1157				.1179	.1179	
5.0	**.0817**	**.1036**											.1127			
6.0														.1179	.1167	
7.0		.1067	0.1084	0.1099	0.1117	0.1125	.1133	.1149		**.1109** .1169			.1169			
8.0		.1073	.1091	.1105	.1117	.1125	.1127	**.1114** .1149		.1151			.1141	.1189	.1185	
9.0		**.1070**					**.1109** .1139									
10.0	**.0851**	.1079	.1099	.1121	.1123	.1125	.1133	.1137		**.1120** .1151			.1189 .1147	.1195 .1207	.1189	.1207
11.0		.1083	.1103	.1105	.1117	.1125	.1145	.1155		.1163			.1153			
12.0		.1101	.1109	.1115	.1135	.1137	.1145	**.1120** .116[illegible]		.1163			.1147	.1207		.1219
13.0		.1095	.1109	.1121	.1135	.1137	**.1140** .1155	.1155		.1169			.1153			
14.0		**.1064**					**.1125**			.1192						
15.0	**.0968**	.1095	.1125	.1127	.1135	.1153	.1149	.1188 .1171	0.1191	.1199 .1175	0.1208	0.1211	.1209	.1223	.1223	.1229
16.0								**.1125** .1165								
17.0							**.1125** .1155	.1188	.1191	.1199	.1202	.1205	.1211	.1212	.1207	
18.0		**.1098**														
19.0	**.0935**															
20.0		.1148	.1164	.1171	.1177	.1178	.1183	.1193 .1186	.1191	.1199 .1208	.1202	.1219 .1217	.1217 .1212			
21.0																
22.0																

23.0							.1184	.1199 .1186	.1202 .1209	*b*.1217						
24.0																
25.0								.1200								
26.0								.1187								

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[a] From the column headed "20 cc" on, in the majority of cases a 24 per cent solution was used diluted to one-half, the resulting strength being the same as that indicated in the table.

[b] Twenty-eight cc of tannin used.

NOTE.—The figures in ordinary type are those of the regular series in which the nitrogen in the tannin solution used was undetermined. The figures in black-faced type do not belong to the regular series. In all of these cases the nitrogen in the tannin used was determined. The fact that these figures are lower than those of the regular series is due to the allowance made for the nitrogen in the tannin, as well as to the fact that different individual tannins were used.

COMPLETENESS OF THE PRECIPITATION OF PEPTONES BY THE TANNIN-SALT REAGENT.

It is, of course, impossible to determine how completely peptones are precipitated by the tannin-salt reagent. It is interesting to know, however, that 15 grams of sodium chlorid and 4 or 5 grams of tannin per 100 cc of solution, which gives the maximum precipitation of proteids, precipitates from 96 to 98 per cent of total nitrogen contained in somatose, which from the nature of its preparation is supposed to consist largely of albumoses with a small amount of peptone. With the same reagent we precipitated about 94 per cent of the total nitrogen contained in Witte's peptone, which is also supposed to consist chiefly of albumoses and peptones, but to contain a larger percentage of peptones than is found in somatose.

The following method of procedure is suggested in the application of the tannin-salt reagent.

MODIFIED TANNIN-SALT METHOD.

In the case of meat powders 1 gram of material is used; in case of solid meat extracts approximately 2 grams of material, and from 10 to 20 cc of liquid or semiliquid extracts should be employed.

The material is transferred to a 100 cc graduated flask. It is dissolved in cold water, and a concentrated sodium chlorid solution added in sufficient quantity to bring the total amount of salt in solution up to the required percentage. The flask is now placed in the ice box at approximately 12° C. after shaking to dissolve the extract. After the solution has reached the ice-box temperature (this requires an hour usually) the required number of cubic centimeters of tannin solution are added. The total volume is now 100 cc. The contents of the flask are thoroughly mixed and the flask returned to the ice box, where it remains overnight. In the morning the solution is filtered at ice-box temperature into a 50 cc graduated flask. The nitrogen is determined in this filtrate, and also in an aliquot portion of the filtrate from a blank, in which the reagents alone are employed. The nitrogen found in the 50 cc multiplied by two gives the total nitrogen in the filtrate, and is subtracted from the total nitrogen in the extract plus the nitrogen found in the tannin solution. The difference is the nitrogen precipitated by the tannin-salt reagent. Fifteen per cent sodium chlorid and 30 cc of 24 per cent tannin have been adopted as giving the most uniform results.

CONCLUSIONS.

It appears from the above that in the application of the tannin-salt method solutions of proteids should be treated with a solution containing about 15 grams of sodium chlorid and 5 grams of tannin per 100 cc. In any case, the solution should not contain less than 10 grams of sodium chlorid and 4 grams of tannin per 100 cc. The precipitation should take place at a low temperature, preferably at from 10° to 15° C. Conducted thus it appears that the tannin-salt method is preferable to any others that have been suggested for the separation of proteoses and peptones from the simpler amido bodies. It yields no precipitates with any of those bodies with the exception of creatin, phenylenediamin, and trimethylamin, and the error occasioned by the precipitation of creatin can be corrected by the determination of that substance.

The other methods which have been used for the separation of proteoses and peptones from the simpler amido bodies are all open to serious objections. Stutzer's phosphotungstic-acid method is unreliable because of the precipitation by that reagent of a wide range of the simpler amido bodies. Mallet's phosphotungstic-acid method, adding a hot solution, is impracticable because of the incomplete precipitation of peptones, and the bromin method has already been discontinued by the association because of its utter unreliability.

The reports of referees having been completed, a discussion took place as to the necessity of condensing these reports and curtailing the discussion owing to the growth in the work of the association and the ever increasing scope and detail of the investigations made. Some members expressed the opinion that the discussion should be limited and others that the statement of the reports should be more concise. It was also suggested by Mr. Wiley that the time covered by the meeting should be extended, and by the president that all desiring to present papers should inform the secretary in advance of the meeting.

The discussion was closed by the adoption of the following resolution offered by Mr. Davidson and amended by Mr. Frear:

Resolved, That the question of presentation of all papers, either by referees or others, be referred to the executive committee for arrangement as to the manner and time of presentation and the time for discussion for the same.

REPORT OF THE COMMITTEE ON THE TESTING OF CHEMICAL REAGENTS.

By L. F. Kebler, *Chairman.*

Since the last meeting of this association little has been reported bearing on the quality of the chemical reagents usually supplied analytical chemists, unless we construe reports bearing on medicinal chemicals as coming within this province. It should be noted in this connection that experience has shown that manufacturers frequently deliver the product customarily sold for medicinal purposes when a C. P. article is called for, and while it is true that the standards for medicinal chemicals are frequently sufficiently exacting to conform to the requirements of a C. P. article, such a practice should be looked upon with disfavor, because it is well known that many of the C. P. goods used for analytical work must have a degree of purity superior to that ordinarily required for a medicinal product.

A new edition of Krauch's "Prüfung der chemischen Reagentien auf Reinheit" has been placed on the market by E. Merck, and the 1890 Pharmacopœia has been superseded by the Eighth Revision, which went into effect September 1, 1905. In many respects the last edition is less exacting than the 1890. This point should be borne in mind by chemists who use the Pharmacopœia as a basis in ordering some of their chemicals.

During the past year the committee has extended its work so as to include eight additional chemicals. The outlines sent out for testing chemical reagents last year are printed in the Proceedings of the Twenty-first Annual Convention of the association.[a] The outlines sent out in 1905 for the additional chemicals are as follows:

HYDROGEN DIOXID.

Physical appearance; number of cubic centimeters of tenth-normal potassium hydroxid required to neutralize acidity of 50 cc by direct titration, using phenolphthalein as indicator. Amount of nonvolatile matter in 50 cc, by evaporation on steam bath and complete drying at 120° C. (Note any foreign odor during or after evaporation.) Test for the presence of salts of aluminum, barium, calcium, iron, lead, magnesium, potassium, and sodium as follows: Evaporate to dryness 25 cc previously rendered alkaline with ammonia water, take up the residue with 25 cc of water, acidulated with hydrochloric acid, and test separate portions for the different metals. No change of color or precipitate should result either immediately or after standing twelve hours when treated with hydrogen sulphid gas, or ammonia water, except when certain metals and a phosphate are present; or when treated with ammonia water and ammonium sulphid except when certain metals and a phosphate are present; or with an ammoniacal portion acidulated with acetic acid, then treated with ammonium oxalate and allowed to stand for twelve hours; or with ammonia water and magnesia mixture; or dilute sulphuric acid and twelve hours standing; or testing with the flame test. Arsenic, render 25 cc alkaline with ammonia water, evaporate to dryness on steam bath, take up residue with dilute sulphuric acid, and treat according to the Marsh-Berzelius method for one hour. Boric acid, Bulletin No. 65, Bureau of Chemistry, page 110, method

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 90, p. 158.

(a). Hydrofluoric acid (U. S. P.). Phosphoric, sulphuric, and hydrochloric acids by the usual tests, using original solution and allowing to stand for twelve hours. Silicate, acidulate 25 cc with hydrochloric acid, evaporate to dryness on steam bath, dry at 100° C. for one hour; the resulting residue should be completely dissolved in 100 cc of 5 per cent hydrochloric acid. Per cent of absolute hydrogen peroxid (U. S. P.). (Each cubic centimeter of tenth-normal potassium permanganate corresponds to 0.00169 gram of hydrogen peroxid.)

OXALIC ACID.

Physical appearance of chemical and 10 per cent aqueous solution; amount and nature of nonvolatile matter on ignition, in 5 grams; sulphate, chlorid, nitrate (by indigo test) in 10 per cent solution, and twelve hours standing. (Acidulate strongly with nitric acid when testing for chlorid.) Phosphate by testing ash in usual manner. Presence of salts of aluminum, calcium, iron, lead, magnesium, potassium, and sodium by methods given under hydrogen dioxid; ammonia, both with sodium hydroxid and Nessler's reagent (Krauch); color of solution when 1 gram of the acid is mixed with 10 cc of concentrated sulphuric acid and gradually heated to 50° C. Per cent purity by titrating with standard solution of potassium permanganate.

POTASSIUM BICHROMATE.

Physical appearance of chemical and of a 10 per cent aqueous solution; loss of weight on heating powder at 120° C. for six hours; chlorid, phosphate, and sulphate in 5 per cent solution after twelve hours standing. (It is necessary to acidulate strongly when testing for sulphate.) Treat a 5 per cent solution with enough alcohol and hydrochloric acid to completely reduce the chromium to the basic condition, test this solution, after dissipating aldehyde and excess of alcohol, by the regular group reagents for aluminum, iron, magnesium, calcium, sodium, and strontium. Per cent of purity by the iodometric method, which consists in liberating free iodin from an iodid by the bichromate in a solution acidulated with sulphuric acid and titrating. (Classen, Ausgewählte Methoden der analytischen Chemie, vol. 1, page 376.) The decinormal factor of potassium bichromate is 0.00487111.

POTASSIUM CARBONATE.

Physical appearance of chemical and of a 10 per cent aqueous solution; moisture at 130° C. for six hours; foreign metals, by outline given under hydrogen dioxid, aluminum, calcium, iron, lead, zinc, magnesium, and sodium; arsenic by Marsh-Berzelius method; chlorid, phosphate, sulphate, silicate, sulphid (Krauch); cyanid and thiosulphate (U. S. P. 1890). Per cent of purity based on anhydrous product, using methyl-orange as indicator.

POTASSIUM PERMANGANATE.

Physical appearance; solubility in water; presence of nitrate (U. S. P.); chlorid and sulphate (Krauch); sodium salt by flame test. Arsenic by Marsh-Berzelius method. (Decolorize aqueous solution containing 5 grams with alcohol, filter, evaporate to dryness on steam bath, take up residue with dilute sulphuric acid, and transfer to generator.) Per cent of purity with oxalic acid.

SILVER NITRATE.

Physical appearance of chemical and of a 10 per cent aqueous solution; reaction to litmus paper; presence of copper, lead, and other foreign salts (U. S. P.). Per cent of purity determined by gravimetric chlorid method.

SODIUM CARBONATE, ANHYDROUS.

Physical appearance of salt and of a 10 per cent aqueous solution; per cent of moisture, drying at 130° C. for six hours; presence of salts of ammonium, aluminum, arsenic, calcium (ammonium oxalate test), lead, and potassium (Krauch); chlorid, phosphate, silicate, sulphate, thiosulphate, and free alkali (Krauch). Per cent of purity based on product as received, using methyl-orange as indicator.

SODIUM THIOSULPHATE.

Physical appearance of chemical and of a 10 per cent aqueous solution; reaction to phenolphthalein; presence of foreign metals in 10 per cent solution; calcium (Krauch); lead, etc. (by hydrogen sulphid); aluminum, iron, etc. (ammonia water and ammonium sulphid). Sulphate (Krauch), iodin solution must be free from sulphate.

Comments on Analytical Results.

ACETIC ACID, GLACIAL, 99.5 PER CENT.

The Bureau of Chemistry did not experience any difficulty during the past year in securing this chemical of the desired degree of purity. The accompanying table, however, shows that a number of such samples were examined. These samples were all purchased previous to the committee's last report. Mr. Kortright reported on two samples, one of which he found of good quality and the other was defective, in that it contained readily oxidizable bodies. He also calls attention to the fact that the stopple in one package was *cork* which had become so soft that it crumbled when removed. The committee desires to lay stress on this point inasmuch as it is quite common to meet with liquid chemicals placed in packages which are closed with improper stopples. A cork stopple should certainly never be employed for any C. P. chemical which is liable to act on it in the process of time.

ETHYL ALCOHOL.

The sample reported on by Mr. Kortright represents the article usually delivered in barrels. Attention was called to the quality of such alcohol last year. It should never be used for analytical purposes without distillation.

AMMONIUM HYDROXID.

It is still common to deliver C. P. ammonia water contaminated with pyridin and even when a special grade is called for the contaminated article is frequently supplied. Sediments are also frequently present but it is only just to say that this is, as a rule, not the fault of the manufacturer, because ammonia water after standing for a considerable length of time acts on the glass, dissolving a portion of the same.

Attention should also be called to the low percentage of actual ammonia contained in the packages usually delivered. It is customary for dealers to mark their product as having a specific gravity of 0.900, which corresponds to approximately 28 per cent of ammonia gas. It is seldom that the material delivered contains this amount of ammonia, as can readily be seen by referring to the table. A number of the samples examined during the year were deficient by over 20 per cent, calculating on a basis of 100. This point was discussed in last year's report.

ETHYL ETHER.

All of the samples examined were of good quality. Attention should be called, however, in this connection to the fact that the eighth revision of the Pharmacopœia allows the presence of 4 cc of water or alcohol, or a mixture of the two in 100 cc of ether, whereas the 1890 Pharmacopœia permitted the presence of only 1 cc in 100 cc of ether.

HYDROCHLORIC ACID.

It is quite common to find this chemical contaminated with free chlorin. A small amount of insoluble matter is also a constant impurity. It is not the desire of this committee to suggest that this chemical should be absolutely free from all impurities, but it is the belief that the nonvolatile matter should not amount to as much as 8.9 mg in 50 cc.

HYDROGEN DIOXID.

Only three brands were examined, two of which were of satisfactory quality, the other containing hydrofluoric acid, which should not be present in a high-grade product.

NITRIC ACID.

All the samples of nitric acid were of good quality with one exception. In this case the amount of nonvolatile matter amounted to 8.9 mg in 50 cc.

Complaint is also sometimes entered because nitric acid is of a yellowish color which is due to the presence of hyponitrous acid. Such a complaint is not well founded, because strong nitric acid is readily converted to a certain degree into hyponitrous acid in the presence of light. Nitric acid should be protected from the light.

OXALIC ACID.

There is certainly room for improvement in the quality of this chemical, as can readily be seen by examining sample No. 179 of the Bureau of Chemistry and the sample reported by Mr. Kortright.

POTASSIUM BICHROMATE.

The quality of this chemical is, as a rule, very good. It is occasionally contaminated with chlorid, sulphate, and phosphate.

POTASSIUM CARBONATE.

There is considerable room for improvement in this chemical. With one exception, all of the samples reported on contain either chlorid or sulphate or both. The fact that one sample was free from these impurities shows that a pure article can be manufactured. It is a question, however, whether a standard should be set which excludes traces of chlorid.

The sample examined by Mr. Kortright is certainly considerably inferior to the goods delivered to the Bureau of Chemistry. As will be noted, his sample contains aluminum, iron, and zinc.

POTASSIUM HYDROXID, BY ALCOHOL.

As a rule this chemical can be obtained of the desired degree of purity without any difficulty. For a major portion of analytical operations it is not necessary to use a chemical which is free from all traces of contamination. If such a chemical is desired it can be prepared from metallic potassium, but the price is such as to preclude its general use in analytical work.

On examining the tables it will be found that sample No. 1113 contains only 79.51 per cent of potassium hydroxid. This is considerably below the standard, which at present is placed at not less than 85 per cent.

POTASSIUM HYDROXID, PURE.

Only one sample of this grade is reported and the results indicate that the sample is of satisfactory quality.

POTASSIUM IODID.

The comments made last year in connection with this chemical are still applicable. There is no difficulty in obtaining a chemical of good quality, but as a rule the article usually delivered is contaminated with some undesirable impurities.

POTASSIUM PERMANGANATE.

This chemical usually contains chlorid or sulphate or both. Inasmuch as it frequently serves as the basis in the preparation of standard volumetric solutions every possible care should be exercised to secure a pure article.

A number of samples examined show that arsenic is by no means an uncommon impurity.

SILVER NITRATE.

This is one of the purest chemicals met with and there should not be any difficulty in securing it of the purity desired for analytical work.

SODIUM CARBONATE.

This is one of the most difficult agents to procure of the proper quality. It is usually contaminated more or less with a chlorid. The point made relative to this impurity in connection with potassium carbonate should also be borne in mind in connection with this chemical. It is frequently far from anhydrous, as can readily be seen by referring to the tabulated results on this chemical. It will also be observed on comparing the analytical results that on adding the per cent of purity and the amount of moisture the sum frequently exceeds 100 per cent. This is due to the fact that the amount of moisture in the various portions of the package is variable and the per cent of moisture and degree of purity were determined in two separate portions of the sample.

SODIUM HYDROXID, BY ALCOHOL.

The remarks made under potassium hydroxid are applicable to this compound. The degree of purity, however, should not fall much below 98 per cent.

SODIUM HYDROXID, PURE.

The article to which the term "pure" is frequently applied is the ordinary commercial product. It is usually claimed to have a purity approximating 98 per cent, but as a rule this claim is not substantiated on analysis.

In the trade channels it is customary to quote this article on the basis of the amount of sodium oxid the article contains, for example, 70, 72, 75, etc. Chemists must admit that the ordinary dealer, not versed in chemical nomenclature, undoubtedly finds it difficult to tell just what is meant when a certain degree of purity is called for. Great care should therefore be exercised when orders are placed to specify distinctly what is wanted.

SODIUM THIOSULPHATE.

There is no difficulty in securing this chemical of the proper degree of purity, but it occasionally happens that the ordinary commercial product is superior to the C. P. article delivered. This is clearly set forth on comparing sample No. 349 with the C. P. articles reported.

Every possible effort should be made to secure this chemical of the highest degree of purity, inasmuch as it frequently forms the basis of standard solutions.

SULPHURIC ACID.

This chemical can usually be obtained of the proper degree of purity, but occasionally a sample is delivered which is contaminated with lead salts. Improperly cleaned bottles are at times used. To require that this chemical be delivered absolutely free from iron, it is believed, would be unreasonable, inasmuch as the conditions attending its manufacture make it practically impossible to entirely eliminate this impurity. This remark is applicable also to other inorganic acids.

TABLE I.—*Acetic acid, glacial, 99.5 per cent.*

Observations.	Analysts, Kebler and Hoover.			
	Serial No. 20.	Serial No. 170.	Serial No. 311.	Serial No. 398.
Quality specified on label	C. P., 99 per cent	Reagent	99.5 per cent	C. P., 99.5 per cent.
Physical appearance	Good	Good	Good	Good.
Sp. gr. at 20° C	1.0534	Undetermined	1.0570	1.054.
Congealing point (° C.)	15	7	13	13.
Per cent acid	99.00	94.52	98.56	98.59.
Miscibility in water and alcohol.	All proportions.	All proportions.	All proportions.	All proportions.
Nonvolatile matter in 50 cc on steam bath.	4 mg	Not determined.	2 mg	1 mg.
Residue on ignition	1 mg	do	Not determined.	Undetermined.
Inorganic acids	Sulphuric	None	None	None.
Empyreumatic material	None	do	do	Do.
Bases	do	do	do	Do.
Reduction of potassium bichromate.	Immediately	Green within 1 min.	Green within 1 min.	Undetermined.
Material reducing $AgNO_3$	None	Undetermined	None	None.
Acetone	do	Present	do	Undetermined.

Observations.	Analysts, Kebler and Hoover.		Analyst, Kortright.	
	Serial No. 716.	Serial No. 1115.	Serial No. 1.	Serial No. 2.
Quality specified on label	C. P., 99.5 per cent.	99.9 per cent	Glacial, C. P., 99.5 per cent.	Glacial, C. P., 99.5 per cent.
Physical appearance	Good	Good	Good	Good.
Sp. gr. at 20° C	1.0548	1.0541	1.0557	1.0515.
Congealing point (° C.)	14.9	14.9	13.7	13.9.
Per cent acid	98.33	98.9	98.62	99.13.
Miscibility in water and alcohol.	All proportions.	All proportions.	All proportions.	All proportions.
Nonvolatile matter in 50 cc on steam bath.	None	None	2.5 mg	1.4 mg (green color).
Residue on ignition	do	do	0.5 mg	0.1 mg.
Inorganic acids	do	do	None	None.
Empyreumatic material	Present	do	do	Do.
Bases	None	do	do	Do.
Reduction of potassium bichromate.	Not within 30 min.	Not within 30 min.	do	Green in less than 1 min.
Material reducing $AgNO_3$	None	None	do	Present.
Acetone	do	do	Trace	Trace.

TABLE II.—*Ammonium hydroxid.*

Observations.	Analysts, Kebler and Hoover.		
	Serial No. 710.	Serial No. 820.	Serial No. 888.
Quality specified on label	Strictly C. P., sp. gr. 0.90.	Strictly C. P., sp. gr. 0.90.	C. P.
Physical appearance	Good	Trace of suspended matter.	Contains sediment.
Sp. gr. at 20° C	0.9062	0.9076	0.9037.
Nonvolatile matter in 50 cc	0.5 mg	0.4 mg	None.
Residue on ignition	None	None	Do.
Acids	do	do	Do.
Bases	do	do	Do.
Empyreumatic material	do	Present	Present.
Per cent ammonia	24.36	25.53	26.05.

Table II.—*Ammonium hydroxid*—Continued.

Observations.	Analysts, Kebler and Hoover.			Analyst, Kortright.
	Serial No. 901.	Serial No. 1100.	Serial No. 1131.	Serial No. 1.
Quality specified on label	C. P., sp. gr. 0.90.	C. P., sp. gr. 0.90.	C. P., sp. gr. 0.90.	Strictly C. P., sp. gr. 0.90.
Physical appearance	Good	Good	Good	Good.[a]
Sp. gr. at 20° C	0.9105	0.9178	0.9208	0.9080.
Nonvolatile matter in 50 cc	1 mg	2.3 mg	2 mg	1.8 mg.
Residue on ignition	None	None	None	1.6 mg.
Acids	do	Trace of carbonic.	do	None.
Bases	do	None	do	Do.
Empyreumatic material	Trace of pyridin	Present	Present	Do.
Per cent ammonia	24.47	21.68	21.28	22.62.[b]

[a] After stopper had been removed there were some small pieces of glass in bottom of bottle.
[b] Per cent titration, using cochineal, 22.44.

Table III.—*Ethyl ether.*

Observations.	Analysts, Kebler and Hoover.		
	Serial No. 724.	Serial No. 815.	Serial No. 889.
Quality specified on label	U. S. P., sp. gr. at 15° C., 0.725.	U. S. P., 1890	U. S. P., 1890.
Physical appearance	Good	Good	Good.
Sp. gr. at 20° C	0.7203	0.725 (at 15° C.)	0.7208.
Miscibility in 95 per cent alcohol and chloroform.	All proportions	All proportions	All proportions.
Boiling point (° C.)	36–55	97 per cent at 36, 3 per cent at 36–55.	36–53.
Foreign odor	Present	Present	Present.
Nonvolatile matter at 100 cc on steam bath.	0.8 mg	None	0.7 mg.
Residue on ignition from steam bath.	None	do	None.
Reaction to litmus	Neutral	Neutral	Neutral.
Acidity in 100 cc to phenolphthalein.	1.7 cc N/100 KOH	1.6 cc N/100 KOH	1.5 cc N/100 KOH.
Aldehyde, etc	Present	Trace	Trace.
Hydrogen peroxid and ozone	None	None	None.
Alcohol and water	Within limit	Within limit	Within limit.

Observations.	Analysts, Kebler and Hoover.		Analyst, Kortright.	
	Serial No. 915.	Serial No. 916.	Serial No. 1.	Serial No. 2.
Quality specified on label	U. S. P., 1890	For anæsthesia	U. S. P., 1890, concentrated.	For anæsthesia.
Physical appearance	Good	Good	Good	Good.
Sp. gr. at 20° C	0.7193	0.7213	0.7200	0.7209.
Miscibility in 95 per cent alcohol and chloroform.	All proportions.	All proportions.	All proportions.	All proportions.
Boiling point (° C.)	Undetermined	Undetermined	34–39	33.8–38.
Foreign odor	None	None	Slight	None.
Nonvolatile matter in 100 cc on steam bath.	4.6 mg	0.8 mg	1 mg	0.4 mg.
Residue on ignition from steam bath.	None	None	Undetermined	Undetermined.
Reaction to litmus	Neutral	Neutral	Neutral	Neutral.
Acidity in 100 cc to phenolphthalein.	6.9 cc N/100 KOH.	3.4 cc N/100 KOH.	2 cc N/100 KOH.	1.5 cc N/100 KOH.
Aldehyde, etc	None	Trace	None	None.
Hydrogen peroxid and ozone	do	None	Present	Do.
Alcohol and water	Within limit	25 cc contains 0.5 cc alcohol or water.	Within limit	Within limit.

TABLE IV.—*Ethyl alcohol, about 95 per cent.*

Observations.	Analysts, Kebler and Hoover.		Analyst, Kortright. Serial No. 1.
	Serial No. 448.	Serial No. 893.	
Quality specified on label	Not specified	Not specified	Not specified.
Physical appearance	Good	Good	Colorless.
Sp. gr. at 20° C	0.8086	0.8188 (at 15°)	0.8211.
Miscibility in water	All proportions	All proportions	All proportions.
Nonvolatile matter in 100 cc on steam bath.	Not weighable	10.6 mg	9 mg.
Residue on ignition	Undetermined	None	0.6 mg.
Fusel oil, aldehyde, and tannin	None	Fusel oil and aldehyde	Aldehyde or tannin.
Furfurol	do	Undetermined	Present.
Reaction to litmus	Neutral	do	Acid.
Acidity to phenolphthalein	100 cc required 1.5 cc N/100 KOH.	100 cc required 16.4 cc N/100 KOH.	100 cc required 22 cc N/100 KOH.

TABLE V.—*Hydrochloric acid.*

Observations.	Analysts, Kebler and Hoover.		
	Serial No. 807.	Serial No. 885.	Serial No. 918.
Quality specified on label	Strictly C. P., sp. gr. 1.20.	C. P	C. P., sp. gr. 1.20.
Physical appearance	Good	Sediment in bottom of bottle.	Slight sediment in bottle.
Sp. gr. at 20° C	1.1880	1.1868	1.1941.
Per cent acid	37.89	37.08	38.85.
Miscibility in water	All proportions	All proportions	All proportions.
Nonvolatile matter in 50 cc on steam bath.	Not weighable	1.8 mg	0.1 mg.
Residue on ignition	None	Undetermined	None.
Foreign acids	do	None	Do.
Bases	do	Iron	Do.
Halogens	do	Free chlorin	Do.
Arsenic	Undetermined	None	Undetermined.

Observations.	Analysts, Kebler and Hoover.			Analyst, Kortright. Serial No. 1.
	Serial No. 972.	Serial No. 1099.	Serial No. 1130.	
Quality specified on label	Strictly C. P., sp. gr. 1.20.	C. P., sp. gr. 1.19.	C. P., sp. gr. 1.19.	Strictly C. P., sp. gr. 1.20.
Physical appearance	Slight sediment in bottle.	Contains black fibrous foreign material.	Good	Good.
Sp. gr. at 20° C	1.1748	1.1833	1.1867	1.180.
Per cent acid	34.25	36.51	36.87	36.17.
Miscibility in water	All proportions.	All proportions.	All proportions.	All proportions.
Nonvolatile matter in 50 cc on steam bath.	3.4 mg	9.2 mg	8.6 mg	1.3 mg.
Residue on ignition	1.8 mg	6.2 mg	0.2 mg	0.1 mg.
Foreign acids	None	None		Sulphuric.
Bases	Trace of iron	Trace of iron	Trace of iron [a]	None.
Halogens	None	Free chlorin	Trace of free chlorin.	Do.
Arsenic	Undetermined	Trace	6 parts per million.	Undetermined.

[a] Test for iron from residue on ignition.

TABLE VI.—*Hydrogen dioxid.*

Observations.	Analyst, Schulz. Serial No. 1007.	Analyst, Hoover. Serial No. 1045.	Analyst, Kortright. Serial No. 1.
Quality specified on label	3 per cent volume	3 per cent volume	Medicinal.
Physical appearance	Clear	Clear	Good.
Acidity (to phenolphthalein) in 50 cc.	5 cc N/10 KOH	6.2 cc N/10 KOH	8.9 cc N/10 KOH.
Nonvolatile matter in 50 cc (dried at 120° C.).	20.5 mg	56 mg	29.1 mg.
Foreign bases	Trace of sodium and iron.	Sodium	Undetermined.
Acids, except phosphoric and boric.	Silicate and chlorid	Silicate, sulphuric, and hydrochloric.	Silicate, HF, HCl, and H_2SO_4.
Phosphoric acid	Present	Present	None.
Boric acid	None	None	Trace.
Arsenic	do	do	None.
Per cent hydrogen peroxid	3.4	3.52	3.79.

TABLE VII.—*Nitric acid.*

Observations.	Analysts, Kebler and Hoover.				Analyst, Kortright.
	Serial No. 886.	Serial No. 973.	Serial No. 1098.	Serial No. 1138.	Serial No. 1.
Quality specified on label.	C. P	C. P., sp. gr. 1.42.	C. P., sp. gr. 1.425.	C. P., sp. gr. 1.425.	Strictly C. P., sp. gr. 1.42.
Physical appearance	Slight brown color.	Good	Slight brown color.	Good	Good.
Sp. gr. at 20° C	1.4225	1.4111	1.4235	1.4129	1.41.
Per cent acid	72.76	68.89	72.35	68.59	69.06.
Miscibility in water	All proportions.	All proportions.	All proportions.	All proportions.	All proportions.
Nonvolatile matter in 50 cc on steam bath.	5.9 mg	1.7 mg	0.7 mg	8.9 mg	1.7 mg.
Residue on ignition	1.4 mg	1.3 mg	0.5 mg	0.4 mg	0.2 mg.
Foreign acids	Trace of hyponitrous.	None	Trace of hyponitrous.	None	Trace of sulphuric.
Bases	Trace of iron.	Trace of iron.	Trace of iron.	Trace of iron.	None.
Halogens	None	None	None	None	Do.
Arsenic	Trace	Undetermined.	Trace	4 parts per million.	Do.

TABLE VIII.—*Oxalic acid.*

Observations.	Analysts, Kebler and Hoover.					Analyst, Kortright.
	Serial No. 178.	Serial No. 179.	Serial No. 489.	Serial No. 809.	Serial No. 965.	Serial No. 1.
Quality specified on label.	Reagent, crystals.	Crystals	C. P	C. P	Reagent, crystals.	Not specified.
Physical appearance.	Good	Contains fibrous foreign material.	Good	Good	Good	Large, clear crystals.
Solution, 10 per cent.	do	Not clear	do	do	do	Clear.
Per cent purity	100.00	95.53	99.37	99.32	100.00	71.47 (anhyd. acid).[a]
Residue on ignition of 5 grams.	None	34.5 mg	Undetermined.	Undetermined.	None	2 mg.
Foreign acids	do	Sulphuric	None	None	do	None.
Bases	do	Trace of iron.	Undetermined.	Undetermined.	do	Al, Fe, K, Mg, Na.
Color of 1 gram with 10 cc conc. sulphuric acid.	No coloration.	Slight yellowish color.	No coloration.	No coloration.	No coloration.	None.

[a] Titrated with standard KOH (phenolphthalein indicator).

TABLE IX.—*Potassium bichromate.*

Observations.	Analysts, Kebler and Hoover.				Analyst, Kortright.	
	Serial No. 210.	Serial No. 211.	Serial No. 511.	Serial No. 1000.	Serial No. 1.	Serial No. 2.
Quality specified on label	Regent	Highest purity.	C. P	C. P	Not specified.	Not indicated.
Physical appearance	Good	Good	Good	Clear crystals.	Good	Do.
Solution 10 per cent	do	do	do	Good	do	Do.
Loss of weight at 120° C. for six hours.	0.019 per cent.	0.051 per cent.	Undetermined.	0.04 per cent.	0.012 per cent.	Do.
Foreign salts	None	None	Trace of chlorid.	Trace of chlorid.	Trace of sulphate and phosphate.	Do.
Per cent purity	100.00	99.63	99.88	99.07	Undetermined.	99.90.

TABLE X.—*Potassium carbonate.*

Observations.	Analysts, Kebler and Hoover.				
	Serial No. 23.	Serial No. 213.	Serial No. 214.	Serial No. 557.	Serial No. 634.
Quality specified on label.	C. P	Reagent	Not specified	C. P	Pure.
Physical appearance	Good	Good	Good	Good	Poor.
Ten per cent aqueous solution.	Contains a few fragments in suspension.	Clear	Clear	Clear	Contains insoluble matter.
Per cent moisture at 130° C. for six hours.	6.8	Undetermined.	15.97	Undetermined.	10.27.
Per cent purity	92.26	96.53	83.39	99.3	88.94.
Foreign salts	Chlorid	Trace of chlorid.	Chlorid and sulphate.	Chlorid	Chlorid and sulphate.
Arsenic	Undetermined.	Undetermined.	Present	Undetermined.	Undetermined.

Observations.	Analysts, Kebler and Hoover.				Analyst, Kortright.
	Serial No. 712.	Serial No. 821.	Serial No. 924.	Serial No. 928.	(*a*)
Quality specified on label.	C. P., from Germany.	C. P	C. P	Reagent	Not specified.
Physical appearance	Good	Contains foreign material.	Good	Good	Good.
Ten per cent aqueous solution.	Clear	Not clear and contains insoluble matter.	Contains insoluble matter.	Clear	Do.
Per cent moisture at 130° C. for six hours.	6.66	9.63	Undetermined.	2.60	7.58.
Per cent purity	92.65	91.28	98.6	99.29[a]	100.50.[b]
Foreign salts	Chlorid	Sulphate	Chlorid	None	Aluminum, iron and zinc, chlorid and sulphate.
Arsenic	None	Present	Undetermined.	do	None.

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[a] Contains caustic.

[b] Based on the anhydrous salt.

TABLE XI.—*Potassium hydroxid, by alcohol.*

Observations.	Analysts, Kebler and Hoover.		
	Serial No. 650.	Serial No. 661.	Serial No. 793.
Quality specified on label	Pure, by alcohol	Strictly C. P., free from H_2SO_4.	By alcohol, made in Germany.
Physical appearance	White sticks	White sticks	White sticks.
Color of 10 per cent alcoholic solution.	Colorless	Colorless, but incompletely soluble.	Colorless, but incompletely soluble.[a]
Per cent alkali	87.65	85.47	85.34.
Foreign metals	Aluminum	Aluminum	Iron and aluminum.
Acids, except carbonates and silicates.	Sulphate and chlorid.	Sulphate and chlorid.	Sulphate and chlorid.
Solubility in water	Good	Good	Good.
Silicates	None	None	None.
Carbonates	Full limit	Within limit	Within limit.
Ammonium compounds	None	None	None.

Observations.	Analysts, Kebler and Hoover.			Analyst, Kortright.
	Serial No. 813.	Serial No. 1047.	Serial No. 1113.	Serial No. 1.
Quality specified on label	By alcohol	By alcohol	By alcohol	Pure, purified by alcohol, sticks.
Physical appearance	White sticks	White sticks	White sticks	Pure white sticks.
Color of 10 per cent alcoholic solution.	Colorless, but incompletely soluble.[a]	Colorless, but incompletely soluble.	Colorless, but incompletely soluble.	Good, colorless.
Per cent alkali	87.28	87.89	79.51	86.64.
Foreign metals	Aluminum	None	Aluminum and trace of iron.	Al, Fe, Ca, Na.
Acids, except carbonates and silicates.	Chlorid. trace of sulphate and phosphate.	Chlorid and trace of sulphate.	Chlorid and sulphate.	Chlorid and trace of sulphate.
Solubility in water	Good	Good	Good	Turbid.
Silicates	None	Present	Present	Present.
Carbonates	Within limit	Within limit	Within limit	More than limit.
Ammonium compounds	None	Trace	None	None.

[a] Becomes slightly yellowish on standing for 48 hours.

TABLE XII.—*Potassium hydroxid, pure.*

Observations.	Analyst, Kortright.	Observations.	Analyst, Kortright.
Quality specified on label	Purified sticks.	Acids, except carbonic and silicic.	Chlorid and sulphate.
Physical appearance	White sticks.	Solubility in water	Good, slightly yellow, 1: 4.
Per cent alkali	85.57.	Silicate	Not indicated.
Foreign metals	Trace of aluminum and iron.	Carbonate	Within limit (U. S. P.).

TABLE XIII.—*Potassium iodid.*

Observations.	Analyst, Hoover.	Analyst, Kortright.	
	Serial No. 840.	Serial No. 1.	Serial No. 2.
Quality specified on label	C. P	C. P., strictly free from iodates.	Not indicated.
Physical appearance	White crystals	Large white crystals	Do.
Solubility in water	Good	Good	Do.
Salts insoluble in alcohol	None	Undetermined	Do.
Alkali in 1 gram	0.16 cc N/10 acid	0.05 cc N/10 acid	Do.
Foreign bases	None	Undetermined	Trace of calcium.
Acids, except iodate	Trace of sulphate	do	More than limit of nitrate and nitrite.
Iodate	None	None	Not indicated.
Cc N/10 silver nitrate required per gram.	59.8	Undetermined	Per cent purity, 99.92.

Table XIV.—*Potassium permanganate.*

Observations.	Analyst, Kebler.			Analyst, Hoover.	Analyst, Kortright.	
	Serial No. 228.	Serial No. 229.	Serial No. 437.	Serial No. 933.	Serial No. 1.	Serial No. 2.
Quality specified on label.	Reagent	Pure crystals.	C. P.	C. P., free from S.	Not indicated.	Not indicated.
Physical appearance.	Good	Good	Dull-brown crystals.	Small dull-brown crystals.	Large crystals.	Do.
Solubility in water.	do	do	Good	Good	Not indicated.	Good.
Foreign salts	None	Chlorid and sulphate.	Chlorid and sulphate.	Chlorid	do	Chlorid and sulphate.
Arsenic	9.00 [a]	5.00 [a]	Undetermined.	4.00 [a]	None	None.
Per cent purity	100.00	99.33	97.14	98.01	Not indicated.	99.80.

[a] Parts per million.

Table XV.—*Silver nitrate.*

Observations.	Analyst, Kebler.	Analyst, Hoover.	Analyst, Kortright.
	Serial No. 348.	Serial No. 897.	Serial No. 1.
Quality specified on label	C. P.	C. P.	Not specified.
Physical appearance	Good	Good	Clear-white crystals.
Aqueous solution, 10 per cent	do	do	Good.
Reaction to litmus	Neutral	Neutral	Neutral.
Foreign salts	None	None	None.
Per cent purity	99.6	99.4	99.9.

Table XVI.—*Sodium carbonate, anhydrous.*

Observations.	Analysts, Kebler and Hoover.				
	Serial No. 335.	Serial No. 336.	Serial No. 514.	Serial No. 570.	Serial No. 655.
Quality specified on label.	Anhyd., C. P.	Anhyd., highest purity.	Anhyd.	Anhyd., highest purity.	Anhyd., C. P.
Physical appearance	Good	Good	Good	Good	Good.
Ten per cent solution.	Clear	Clear	Turbid, contains foreign material.	Impurities in suspension.	Clear.
Per cent purity	99.6 [a]	96.09	85.03	98.79	94.77.
Per cent moisture, drying at 130° C. for 6 hours.	0.9	3.99	17.28	3.24	4.7.
Foreign salts	None	None	Chlorid	Chlorid	Sulphate.
Free alkali	do	do	None	None	None.

Observations.	Analysts, Kebler and Hoover.					Analyst, Kortright.
	Serial No. 668.	Serial No. 895.	Serial No. 956.	Serial No. 1048.	Serial No. 1135.	
Quality specified on label.	Anhyd., C. P.	Anhyd., highest purity.	Anhyd., reagent.	Anhyd., C. P.	Anhyd., C. P.	Not indicated.
Physical appearance.	Good	Good	Good	Dirty white	Creamy white.	Fine white powder.
Ten per cent solution.	Clear	Slightly turbid, with insoluble residue.	Clear	Dirty-yellowish color.	Clear	Good.
Per cent purity	94.27	84.24	99.16	91.12	96.88	97.05.
Per cent moisture, drying at 130° C. for 6 hours.	5.23	16.21	1.09	8.53	2.27	3.31.
Foreign salts	None	Chlorid	None	Silicate, sulphate, and chlorid.	Chlorid.	Traces of Fe, K, silicate, and sulphate.
Free alkali	do	None	Present	None	None	Present.

[a] After drying.

TABLE XVII.—*Sodium hydroxid, by alcohol.*

Observations.	Analyst, Hoover.		Analyst, Kortright.
	Serial No. 782.	Serial No. 1001.	Serial No. 1.
Quality specified on label	Sticks, pure by alcohol.	By alcohol	Pure, purified by alcohol.
Physical appearance	White sticks	White sticks	Pure white sticks
Solubility in water	Good	Good	Good.
Color of 10 per cent alcoholic solution.	Colorless	Colorless, but incompletely soluble.	Do.
Per cent of alkali	98.58	97.46	98.04.
Foreign bases	None	None	Aluminum, iron, and calcium.
Acids, except carbonates	Trace of chlorid and sulphate.	Trace of chlorid	Trace of phosphate; more than limit of chlorid.
Ammonium compounds	None	None	None.
Carbonate	Within limit	Trace	More than limit.
Calcium	None	None	Trace.

TABLE XVIII.—*Sodium hydroxid, pure.*

Observations.	Analysts, Kebler and Hoover.				Analyst, Kortright.
	Serial No. 659.	Serial No. 725.	Serial No. 791.	Serial No. 923.	Serial No. 1.
Quality specified on label.	98 per cent	98 per cent	98 per cent	98 per cent	Purified sticks.[a]
Physical appearance	White lumps	White powder.	White powder.	White powder.	Cream-white sticks.
Solubility in water	Turbid and contains residue.	Fair, but contains residue.	Contains mechanical impurities.	Turbid and contains residue.	Colorless at first, yellowish after 2 days.
Per cent alkali	74.95	93.71	94.86	92.25	94.48.
Foreign bases	Iron	Aluminum	Iron and aluminum.	Iron	Trace of iron and aluminum.
Foreign acids, except silicates and carbonates.	Sulphate and chlorid.	Sulphate and chlorid.	Sulphate and chlorid.	Sulphate and chlorid.	None indicated.
Silicates	Present	Present	Present	Present	Excess of limit U. S. P.
Carbonates	Full limit	Full limit	Full limit	Full limit	Full limit, U. S. P.

[a] Contains arsenic.

TABLE XIX.—*Sodium thiosulphate.*

Observations.	Analyst, Kebler.			Analyst, Hoover.		Analyst, Kortright.
	Serial No. 332.	Serial No. 349.	Serial No. 419.	Serial No. 690.	Serial No. 839.	Serial No. 1.
Quality specified on label.	C. P., crystals.	Com'l	C. P	C. P	C. P	Not specified.
Physical appearance.	Like com'l product.	Good	Slightly damp.	Good	Good	Good.
Solution, 10 per cent.	Contains fragments.	do	Slightly opalescent.	do	do	Do.
Reaction to phenolphthalein.	Alkaline	Neutral	Neutral	Neutral	Neutral	Alkaline.
Foreign bases	Trace of iron	None	None	None	None	None.
Acids	Trace of chlorid.	do	do	Trace of sulphate.	do	Trace of sulphate.
Per cent purity.	100.53	99.13	100.20	98.68	98.45	Not indicated.

Table XX.—*Sulphuric acid.*

Observations.	Analysts, Kebler and Hoover.					Analyst, Kortright.
	Serial No. 718.	Serial No. 845.	Serial No. 887.	Serial No. 948.	Serial No. 1087.	Serial No. 1.
Quality specified on label.	Strictly C. P., sp. gr. 1.84.	Strictly C. P., sp. gr. 1.84.	C. P.	C. P.	C. P.	Strictly C. P., sp. gr. 1.84.
Physical appearance.	Good	Slight sediment.	Contains sediment.	Contains black particles.	Good	Clear, colorless.
Sp. gr. at 20° C.	1.839	1.83	1.8385	1.8388	1.8381	1.8333.
Per cent acid.	95.25	95.57	95.71	95.81	94.07	94.25.
Residue on ignition in 50 cc.	None	10.5 mg	56.0 mg	3.0 mg	Undetermined.	0.4 mg.
Miscibility in water and in 95 per cent alcohol.	All proportions.	All proportions.	Turbid in alcohol.	All proportions.	All proportions.	Complete.
Foreign acids	None	None	None	None	None	None.
Bases	do	Trace of iron.	Lead and iron.	Trace of iron.	do	Do.
Halogens	do	None	None	None	do	Do.
Ammonium compounds.	do	do	do	do	do	Do.
Arsenic	Undetermined.	Undetermined.	do	Undetermined.	do	Do.

REPORT OF COMMITTEE ON THE UNIFICATION OF TERMS FOR REPORTING ANALYTICAL RESULTS.

By R. J. Davidson, *Chairman.*

The committee had several meetings and did considerable work, as a result of which an unnumbered circular was issued by the Bureau of Chemistry in September giving tentative schedules for the subjects of soils, fertilizers, ash, sugars, feeding stuffs, foods, and insecticides. The committee was unanimous on these subjects with the exception of those of soils and ash, and the two views developed were set forth by Mr. Hopkins and Mr. Fraps. In a work of this kind differences of opinion are to be expected, and therefore about four hundred copies of this circular were sent out for criticism before the committee decided on the recommendations to be made to the association. On the first page of the circular mentioned the following statement was made:

> In presenting its report at the next meeting of the association the committee desires to represent as fully as possible the ideas of the majority of the members of the association and to place before the association in printed form as many reasons as possible both for and against all recommendations that they may make, and with this in view the report of the committee, so far as it has been prepared, is presented herein, with the request that all who receive it will write in full to the chairman of the committee, Mr. R. J. Davidson, of Blacksburg, Va., and present their opinions regarding the recommendations here presented, and criticise the report in detail.

It was hoped that a large number of replies would be received, but only six chemists out of the 400 addressed sent any criticism to the chairman. On this account the committee does not feel that it is in a position to make any recommendation, but it is expected that every member of the association will give an opinion on the preliminary report during 1906.

It is recommended, therefore, that the work be continued for another year.

Upon motion by Mr. Van Slyke the report was approved and the committee continued.

REPORT OF COMMITTEE ON THE UNIFICATION OF SOIL METHODS.

By L. L. Van Slyke.

Your committee appointed to consider a plan for the unification of soil methods has given the matter careful consideration and submits the following report:

The only feasible plan of accomplishing the desired results is, we believe, in the line of the traditions established by the association, viz, studying all proposed new methods through referees, supplemented by special work in individual laboratories, the methods examined to stand or fall by the results reached.

In the present transitional stage of soil analysis and its interpretation the committee suggests that conservatism should be observed in putting forward new methods of soil analysis which can be regarded as radical, unless supported by careful work of a convincing character. Every encouragement should be offered to promote the study of methods of soil analysis in relation to the interpretation of the results as bearing on soil fertility. Every new method or modification proposed must be regarded as simply on probation until studied by the association, the official methods remaining, as far as possible, the standard of comparison. The committee requests that it be discharged from further action.

L. L. Van Slyke.
Frank Cameron.
H. J. Wheeler.

REPORT OF THE COMMITTEE ON THE DEFINITION OF PLANT FOOD.

By H. W. Wiley.

During the past year the committee on the definition of plant food appointed by this association has carried on an extensive correspondence with the similar committee representing the botanists of the United States as appointed by the botanical section of the American Association for the Advancement of Science. That committee comprised the following members: C. R. Barnes, University of Chicago; F. C. Newcomb, University of Michigan; D. T. McDougal, New York Botanical Garden; H. M. Richards, Columbia University, and B. E. Livingston, University of Chicago.

The proposed definitions as agreed upon by the chemists and the botanists, respectively, together with the explanatory remarks on the same of the chairmen of the two committees, are as follows:

(1) Definition Proposed by Chemists.

The term "plant food" includes the substances entering the plant from without, which are necessary to its nourishment, and which therefore perform essential, physiological functions in its growth.

Comments by Dr. H. W. Wiley: These functions may consist in the nourishment of the tissues of the plant, or in establishing the necessary conditions for the circulation of fluids in the plant, or in inducing catalytic reactions. The organic substances which are formed within the plant and which may be transported from one part of the plant to another, with or without change, or which when stored in the seed may be consumed in the germination of the new plant, shall not be considered as ordinary plant foods. These materials are reserve substances which are used in such a way in germination that the material formed from them is only another form of plant tissue itself. In other words, plants can not be considered as autophagous.

(2) Definition Proposed by Botanists.

Plant food is merely a convenient expression, not permitting precise definition of universal applicability. In general, plant food consists of those carbon compounds used by the plant for the construction of its body or as a source of energy. The food either enters the body from without, or is made within it, out of such materials as gases, water, and mineral salts.

Comment by Professor Barnes: I must confess that I do not see the ground on which the chemists can stand scientifically in assuming to make a definition of a physiological term. * * * If you admit that the food of animals is organic, that an etiolated seedling and other chlorophyll-free plants require organic food, the remainder of the question becomes purely botanical, and the botanists certainly ought to be better able to determine the matter touching green plants than the chemists. We are ready, however, to hear any arguments and shall be interested to see how you will undertake to prove that the food of a cell containing chlorophyll is inorganic, while that of its colorless next door neighbor in the leaf is organic; that the food of nine-tenths of a green plant (the chlorophyll-free part) is organic, while that of the other tenth (the chlorophyllus part) is inorganic; that the food of chlorophyllus cells suddenly changes upon the withdrawal of light (I suppose you would not contend that these cells do not require food during periods of darkness) from inorganic to organic.

It would appear also that you wish to include oxygen among foods. This is a still more futile proposition, since all the later studies of respiration tend to show that it is a process of hydroxylation and that free oxygen is not necessary for the release of energy, but is only incidental to the maintenance of the conditions which permit its release.

It is not worth while to enter upon the question of whether food must enter from the outside until we settle some of the fundamental questions. I think you would find it difficult to maintain that thesis.

It is thus seen that a very clear line of difference has been developed between the two committees. Your committee is of the opinion that plant food is a term which should be applied to bodies entering the organism of the plant from without, and taking part in its metabolic activity, whether these bodies be organic or inorganic in character.

The definition of the committee of the botanists of plant food includes only the materials which are taken into the plant and modified therein into forms suitable for building tissue and supporting the other metabolic activities of the plant. In other words, the botanists deem the name plant food to apply to such substances as water, carbon dioxid, phosphorus, nitrogen, lime, iron, etc., and confine the expression plant food to the products of botanical synthesis, either alone or in combination with organic nitrogen and sulphur bodies.

Your committee is not willing to yield its opinion in this respect, and it seems hardly possible that the botanists will yield theirs. We, therefore, recommend that the committee be continued and instructed to confer further with the botanists, and if no common ground for a definition can be found, that a definition of plant food be reported by your committee for consideration at the next meeting.

The report was approved and the committee continued.

Mr. Ross introduced the following resolution, which was referred to the committee on fertilizer legislation:

Resolved, That the fertilizer control officials be urged to require inspectors to use in sampling the method recommended in the report of the uniform legislation committee published in the Proceedings of the fifteenth meeting of the association.[a] The method is the same as that adopted by the Hot Springs meeting of commissioners of agriculture, and is now in use in many States.

Doctor Wiley called attention to the fact that it was possible that the Association of Agricultural Colleges and Experiment Stations might meet in California in 1906, and suggested that the authority to choose the place of meeting for the Association of Official Agricultural Chemists be delegated to the executive committee, that arrangements might be made for the two associations to meet in the same place according to the usual practice, if deemed practicable. Doctor Wiley also called attention to the fact that invitations had been received from boards of trade and associations in Chicago, Asheville, N. C., Denver, Colo., and several cities in California to hold the 1906 meeting in those respective localities.

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[a] U. S. Dept. Agr., Bureau of Chemistry, 1899, Bul. 56, p. 131.

Mr. Van Slyke objected, on the ground that the meetings held outside of Washington had never had as large an attendance nor accomplished as much work as when the usual meeting place was chosen, and, viewing the matter from the single point of view of the best interests of the work of the association, made the motion that the next meeting to be held in Washington.

Mr. Hare, Mr. Scovell, and Mr. Ross spoke in favor of occasionally changing the place of meeting, and the following motion, offered by Mr. Scovell, was passed:

Resolved, That the place of meeting for the next convention of the association be made discretionary with the executive committee.

The secretary was instructed to thank the various authorities who had invited the association to meet in their respective cities.

The association adjourned.

OFFICERS, REFEREES, AND COMMITTEES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR THE YEAR 1906.

President.

Mr. C. G. Hopkins, Urbana, Ill.

Vice-President.

Mr. John P. Street, New Brunswick, N. J.

Secretary.

Mr. H. W. Wiley, Washington, D. C.

Additional members of Executive Committee.

Mr. Harry Snyder, St. Anthony Park, St. Paul, Minn.
Mr. M. B. Hardin, Clemson College, S. C.

Referees.

Phosphoric acid: B. W. Kilgore, Raleigh, N. C.
Nitrogen:
  Determination of nitrogen: J. H. Gibboney, Blacksburg, Va.
  Separation of nitrogenous bodies: R. Harcourt, Guelph, Canada (milk and cheese proteids).
Potash: A. L. Knisely, Corvallis, Oreg.
Soils: J. H. Pettit, Urbana, Ill.
Dairy products: F. W. Woll, Madison, Wis.
Foods and feeding stuffs: J. K. Haywood, Washington, D. C.
Food adulteration: A. E. Leach, Boston, Mass.
Sugar: C. A. Browne, jr., Audubon Park, La. (Special analytical methods.)
Tannin: H. C. Reed, Stamford, Conn.
Insecticides: G. E. Colby, Berkeley, Cal.
Inorganic plant constituents: W. W. Skinner, Washington, D. C.
Medicinal plants and drugs: L. F. Kebler, Washington, D. C.

Associate Referees.

Phosphoric acid: J. M. McCandless, Atlanta, Ga.
Nitrogen:
  Determination of nitrogen: C. L. Penny, Newark, Del.
  Separation of nitrogenous bodies—
    Meat proteids: F. C. Cook, Washington, D. C.
    Vegetable proteids: Harry Snyder, St. Paul, Minn.
Potash: B. B. Ross, Auburn, Ala.
Soils: S. D. Averitt, Lexington, Ky.
Dairy products: J. M. Bartlett, Orono, Me.
Foods and feeding stuffs: John P. Street, New Brunswick, N. J.
Food adulteration:
  (1) Colors: E. F. Ladd, Agricultural College, N. Dak.
  (2) Saccharine products, including confectionery: C. H. Jones, Burlington, Vt.
  (3) Fruit products: H. C. Lythgoe, Boston, Mass.
  (4) Wine: Julius Hortvet, St. Paul, Minn.
  (5) Beer: H. E. Barnard, Indianapolis, Ind. (General associate on food adulteration.)
  (6) Distilled liquors: C. A. Crampton, Washington, D. C

(7) Vinegar: R. B. Fitz Randolph, Trenton, N. J.
(8) Flavoring extracts: E. M. Chace, Washington, D. C.
(9) Spices: A. L. Winton, New Haven, Conn.
(10) Baking powder and baking chemicals: W. M. Allen, Raleigh, N. C.
(11) Meat and fish: E. L. Redfern, Lincoln, Nebr.
(12) Fats and oils: L. M. Tolman, Washington, D. C
(13) Dairy products: A. E. Leach, Boston, Mass.
(14) Cereal products: A. McGill, Ottawa, Canada.
(15) Infants and invalids' foods: W. D. Bigelow, Washington, D. C.
(16) Vegetables: H. V. Tartar, Portland, Oreg.
(17) Condiments other than spices: R. E. Doolittle, New York.
(18) Cocoa and cocoa products: E. M. Bailey, New Haven, Conn.
(19) Tea and coffee: C. D. Howard, Concord, N. H.
(20) Preservatives: W. L. Dubois, Washington, D. C.
(21) Determination of water in foods: F. C. Weber, Washington, D. C.

Sugar:
Molasses methods: J. E. Halligan, Baton Rouge, La.
Chemical methods: L. S. Munson, Washington, D. C.

Tannin: F. P. Veitch, Washington, D. C.
Insecticides: W. B. Ellett, Blacksburg, Va.
Inorganic plant constituents: John W. Ames, Wooster, Ohio.
Medicinal plants and drugs: Charles H. La Wall, Philadelphia, Pa.

SPECIAL COMMITTEES.

Food Standards.

Mr. William Frear, State College, Pa., chairman.
Mr. H. W. Wiley, Washington, D. C.
Mr. H. A. Weber, Columbus, Ohio.
Mr. M. A. Scovell, Lexington, Ky.
Mr. E. H. Jenkins, New Haven, Conn.

Fertilizer Legislation.

Mr. H. W. Wiley, Washington, D. C., chairman.
Mr. B. W. Kilgore, Raleigh, N. C.
Mr. H. B. McDonnell, College Park, Md.
Mr. H. A. Huston, St. Louis, Mo.
Mr. B. B. Ross, Auburn, Ala.

Testing Chemical Reagents.

Mr. L. F. Kebler, Washington, D. C., chairman.
Mr. A. L. Winton, New Haven, Conn.
Mr. B. W. Kilgore, Raleigh, N. C.

Unification of Terms for Reporting Analytical Results.

Mr. R. J. Davidson, Blacksburg, Va., chairman.
Mr. C. G. Hopkins, Urbana, Ill.
Mr. W. D. Bigelow, Washington, D. C.
Mr. G. S. Fraps, College Station, Tex.
Mr. C. A. Browne, jr., Audobon Park, New Orleans, La.

Definition of "Plant Food."

Mr. H. W. Wiley, Washington, D. C., chairman.
Mr. H. J. Wheeler, Kingston, R. I.
Mr. L. L. Van Slyke, Geneva, N. Y.
Mr. E. W. Magruder, Richmond, Va.
Mr. B. W. Kilgore, Raleigh, N. C.

CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

(1) This association shall be known as the Association of Official Agricultural Chemists of the United States. The objects of the association shall be (1) to secure uniformity and accuracy in the methods, results, and modes of statement of analysis of fertilizers, soils, cattle foods, dairy products, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

(2) Analytical chemists connected with the United States Department of Agriculture, or with any State or national agricultural experiment station or agricultural college, or with any State or national institution or body charged with official control of the materials named in section 1, shall alone be eligible to membership; and one such representative for each of these institutions or boards, when properly accredited, shall be entitled to enter motions or vote in the association. Only such chemists as are connected with institutions exercising official fertilizer control shall vote on questions involving methods of analyzing fertilizers. All persons eligible to membership shall become members ex-officiis and shall be allowed the privileges of membership at any meeting of the association after presenting proper credentials. All members of the association who lose their right to such membership by retiring from positions indicated as requisite for membership shall be entitled to become honorary members and to have all privileges of membership save the right to hold office and vote. All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall not be entitled to enter motions or vote.

(3) The officers of the association shall consist of a president, a vice-president, and a secretary, who shall also act as treasurer; and these officers, together with two other members to be elected by the association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board whose members are eligible to membership, his office shall be considered vacant, and a successor may be appointed by the executive committee, to continue in office till the annual meeting next following.

(4) There shall be appointed by the executive committee, at the regular annual meeting, a referee and such associate referees for each of the subjects to be considered by the association as that committee may deem appropriate.

It shall be the duty of these referees to prepare and distribute samples and standard reagents to members of the association and others desiring the same, to furnish blanks for tabulating analyses, and to present at the annual meeting the results of work done, discussion thereof, and recommendations of methods to be followed.

(5) The special duties of the officers of the association shall be further defined, when necessary, by the executive committee.

(6) The annual meeting of this association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

(7) No changes shall be made in the methods of analysis used in official inspection, except by unanimous consent, until an opportunity shall have been given all official chemists having charge of the particular inspection affected to test the proposed changes.

(8) Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any meeting, regular or special, seven enrolled members entitled to vote shall constitute a quorum for the transaction of business.

(9) The executive committee will confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the association.

(10) All proposed alterations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by the approval of two-thirds of the members present entitled to vote.

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